

DECLARRATION

I, Yukiko HAYASHI, the translator of the attached document, do hereby certify that to the best of my knowledge and belief the attached document is a true English translation of Japanese Patent Application No. 2003-014045.

Signed, this ninth day of November, 2005

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ne of Documentl Application for Patent Reference No.] 0209401 [Date of Filing] January 22, 2003 [Addressee] Commissioner of Japan Patent Office 5 [Int'l Class] G03G 9/087 [Title of the Invention] Toner and Image Forming Apparatus [Number of Claims] 23 [Inventor] [Address] c/o Ricoh Company, Ltd., 10 3-6, Nakamagome 1-chome, Ota-ku, Tokyo [Name] Masami Tomita [Inventor] [Address] c/o Ricoh Company, Ltd., 3-6, Nakamagome 1-chome, Ota-ku, Tokyo [Name] Toshiki Nanya [Inventor] [Address] c/o Ricoh Company, Ltd., 20 3-6, Nakamagome 1-chome, Ota-ku, Tokyo [Name] Fumihiro Sasaki [Inventor] [Address] c/o Ricoh Company, Ltd., 25 3-6, Nakamagome 1-chome, Ota-ku, Tokyo [Name] Shigeru Emoto [Inventor] [Address] c/o Ricoh Company, Ltd., 30 3-6, Nakamagome 1-chome, Ota-ku, Tokyo [Name] Shinichiro Yaqi [Inventor] [Address] c/o Ricoh Company, Ltd., 35 3-6, Nakamagome 1-chome, Ota-ku, Tokyo [Name] Hiroto Higuchi [Inventor] [Address] c/o Ricoh Company, Ltd.,

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20 [Payment Method] Prepayment

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[List of Attached Documents]

[Name of Document] Specification 1

25 [Name of Document] Drawing 1

[Name of Document] Abstract 1

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[Necessity of Proof] Necessary

[Name of Document] Specification

30 [Title of the Invention] Toner and Image Forming Apparatus

[Scope of Claims]

[Claim 1] Dry toner comprising at least a toner binder, a colorant, and wax, characterized in that the wax is included in

a toner particle in a form of fine particle and exists throughout a part adjacent to a surface and an inner part of the toner particle, and density of the wax existing adjacent to the surface of the toner particle is greater than density of the wax existing in the inner part of the toner particle.

[Claim 2] The dry toner according to claim 1, characterized in that an occupied area ratio of the wax is between 5 to 40 % in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particle.

[Claim 3]

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The dry toner according to claim 1 or 2, characterized in that the wax is internally included in the toner particle in a form of fine particle, and an amount of wax existing in the toner particle in the portion on the arbitral cross-section having the center of the toner particle thereon, wherein the portion is positioned between the circumference of the arbitral cross-section and the inner circumference having the radius which is two-thirds of the radius of the toner particle, is 70 % by number or more relative to the entire wax existing in the toner particle.

[Claim 4] The dry toner according to any one of claims 1 through 3, characterized in that the wax is not exposed on the surface of the toner particle.

[Claim 5] The dry toner according to any one of claims 1 through 4, characterized in that 70 % by number or more of a dispersed wax particle dispersedly existing inside the toner particle has a diameter of 0.1 to 3 μ m.

[Claim 6] The dry toner according to any one of claims 1 through 5, characterized in that a content of the wax in the toner is 3 to 10 parts by weight % relative to 100 parts by weight % of a component of resin.

[Claim 7] The dry toner according to any one of claims 1 through 6, characterized in that any one of or in combination of free fatty acid eliminated camauba wax, rice wax, montan wax, and ester wax are used as the wax.

[Claim 8] The dry toner according to any one of claims 1 through 7, characterized in that modified polyester (i) is included as the toner binder.

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[Claim 9] The dry toner according to any one of claims 1 through 8, wherein the dry toner may be obtained by dissolving or dispersing a toner composite including the modified polyester (i) in an organic solvent, and then dispersing in an aqueous solvent.

[Claim 10] The dry toner according to any one of claims 1 through 9, wherein the dry toner may be obtained by generating polyester having a urea bonding in a process of dissolving or dispersing a toner composite including a pre-polymer in the organic solvent, and then dispersing in the aqueous solvent.

[Claim 11] The dry toner according to any one of claims 1 through 10, characterized in that the toner binder comprises unmodified polyester (LL) as well as the modified polyester (i), and that a weight ratio of the (i) to the (LL) is between 5/95 to 80/20.

[Claim 12] The dry toner according to any one of claims 1 through 11, characterized in that a peak molecular weight of the toner binder is 1000 to 10000.

[Claim 13] The dry toner according to any one of claims 1 through 12, characterized in that glass transition temperature (Tg) of the toner binder is between 40 to 70 $^{\circ}$ C.

[Claim 14] The dry toner according to any one of claims 1 through 13, characterized in that a volume average particle diameter (Dv) of the toner is between 3.0 to 8.0 μ m, and a ratio of the volume average particle diameter to a number average diameter (Dn) Dv/Dn is between 1.00 to 1.20.

[Claim 15] The dry toner according to any one of claims 1 through 14, characterized in that an average circularity of the toner is

between 0.93 to 1.00.

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[Claim 16] The dry toner according to any one of claims 1 through 14, characterized in that a particle of the toner has a spindle shape.

[Claim 17] The dry toner according to any one of claims 1 through 14 or 16, characterized in that the particle of the toner has a spindle shape, a ratio of a major axis r1 to a minor axis r2 (r2/r1) may be expressed as between 0.5 to 0.8, and a ratio of thickness r3 to the minor axis r2 (r3/r2) may be expressed as between 0.7 to 1.0.

[Claim 18] An image forming apparatus for fixing a toner image on a transfer member by passing the transfer member between two rollers and thereby heating and fusing the toner image, characterized in that the image forming apparatus comprises a fixing device for fixing at surface pressure applied between two rollers (roller load/contact area) of 1.5×10^5 Pa or less.

[Claim 19] The image forming apparatus according to claim 18, characterized in that the fixing device comprises a heating member having a heat emitting member, a film contacting the heating member, and a pressing member press-contacting the heating member via the film, wherein a recording medium on which an unfixed image is formed is passed between the film and the pressing member to be fixed by heat.

[Claim 20] The image forming apparatus according to claim 18 or 19, characterized in that a photoconductor used for image formation is an amorphous silicon photoconductor.

[Claim 21] The image forming apparatus according to any one of claims 18 through 20, characterized by comprising a development means including an electric field printing means for applying an alternating electric field when developing a latent image on the photoconductor.

[Claim 22] The image forming apparatus according to any one of claims 18 through 21, characterized by comprising a charging device

for charging by causing a latent image carrier to contact a charging member, and applying voltage on the charging member.

[Claim 23]

A process cartridge integrally supporting a photoconductor, and at least one means selected from a group of a charging means, a development means, and a cleaning means, and is attachable to or detachable from an image forming apparatus, characterized in that the development means comprises toner according to any one of claims 1 through 17.

[Detailed Description of the Invention]

[0001]

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[Technical Field of the Invention]

The present invention relates to toner for use in a developer for developing an electrostatic image in electrophotography, electrostatic recording, electrostatic printing, and so forth, and an electrophotography development device using the toner. More specifically, the present invention relates to toner, a developer, a development device for electrophotography for use in a copier, a laser printer, a facsimile for plane paper, and so forth, using a direct or indirect electrophotographic development method. Further, the present invention relates to a toner agent for electrophotography, an image forming apparatus (development device), and a process cartridge for use in a full-color copier, a full-color laser printer, a full-color facsimile for plane paper using a direct or indirect electrophotographic multicolor development method.

[0002]

[Background Art]

A developer for use in electrophotography, electrostatic recording, electrostatic printing, and so forth, temporarily adheres on an image carrier such as a photoconductor, for instance, on which an electrostatic image is formed in a development process. Then the developer is transferred from the photoconductor to a

transfer medium such as transfer paper in a transfer process, and is fixed on the transfer medium in a fixing process. As a developer for developing the electrostatic image formed on an latent image holding surface, a two-component type developer including a carrier and toner, and a one-component type developer which do not require the carrier (magnetic toner, non-magnetic toner) are known. As dry toner used in the electrophotography, the electrostatic recording, the electrostatic printing, and so forth, toner formed of by melting and kneading a toner binder (binder resin) such as a styrene resin and polyester with a colorant, and then pulverizing a resulting mixture is conventionally used.

[0003]

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After the dry toner is transferred on paper, and so forth, for development, the dry toner is fixed by heating and melting by using a heat roller. In this case, when temperature of the heat roller is too high, a problem (hot offset) that the toner excessively melts and adheres on the heat roller occurs. In addition, when the temperature of the heat roller is too low, a problem arises in that the toner does not sufficiently melt, resulting in insufficient fixing. Accordingly, there is a demand in toner having higher temperature to cause the hot offset (excellent hot offset (excellent fixing temperature resistance) and low characteristic at low temperature), while energy conservation and downsizing of a device such as a copier are considered. In addition, the toner is required to have heat-resistant storage stability such that blocking of toner is not caused when the toner is stored or at ambient temperature in a device. Particularly, in a full-color copier and a full-color printer, since glossiness and a color mixing property of an image is required, it is necessary for the toner to have lower melting viscosity. Consequently, a polyester toner binder exhibiting sharp melting characteristic is used. However, hot offset is likely to occur with such toner. Accordingly, in a full-color device, silicone oil, and so forth, is conventionally

applied on the heat roller. At the same time, an oil tank and an oil applying device are required in a method of applying silicone oil on the heat roller. Accordingly, the device becomes complex and large in size. In addition, with the method, the heat roller is caused to be deteriorated and maintenance per certain period is required. Further, it is unavoidable that oil adheres on copy paper, a film for an OHP (overhead projector), and so forth. Particularly in the OHP, there is a problem such that the adhered oil deteriorates a color tone.

[0004]

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To prevent toner fusion without applying the oil on the heat roller, a method of adding wax in the toner is generally used. Releasing effect of the method is largely affected by a condition of dispersed wax in the binder. When the wax is compatible with the binder, a releasing characteristic of the wax may not be developed. The releasing characteristic of the wax may be improved only when the wax exist as a incompatible domain particle. When a dispersion diameter of the domain particle is too large, a ratio of wax existing adjacent to a surface of the toner particle relatively increases. Consequently, the toner exhibits an aggregation characteristic, lowering fluidity. Further, filming is caused due to the wax or a carrier transfers onto a photoconductor during long-term use. Accordingly, a problem such that an image with favorable quality is prevented from being achieved. addition, in a case of color toner, color reproducibility and transparency are impaired. On the contrary, when the dispersion diameter is too small, the wax is excessively and finely dispersed and the releasing characteristic may not be sufficiently achieved. As described above, even though it is essential to control the dispersion diameter of the wax, an appropriate control method is not yet found. Particularly, in a case of toner manufactured by a pulverization method, a significant factor in determining the dispersion diameter is sheer force of kneading during melting and kneading. A polyester resin which is often used for toner binder in recent years is low in viscosity, and consequently, the shear force of kneading may not be applied. Accordingly, it is very difficult to control the dispersion diameter of the wax to obtain an adequate dispersion diameter.

In addition, another problem of the pulverization method is that an amount of wax to be exposed on a surface may be increased because of the wax is likely to have a fracture surface.

[0005]

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To achieve a high quality image, an attempt is made to improve toner by reducing a toner particle diameter or by narrowing a particle size distribution. However, a form of a particle obtained is conventional manufacturing method with Consequently, the toner is further pulverized by being agitated with carrier in a development part in a machine, or by contact stress between the toner and a development roller, a toner supply roller, a layer thickness regulation blade, a frictional charging blade, and so forth, when the toner is used as a one-component type developer. Accordingly, an extremely fine particle may be generated or a fluidizer is embedded on a surface of the toner. As a result, a phenomenon of deterioration of image quality occurs. In addition, fluidity of the toner as a powder body is poor because of a shape of the toner particle. Accordingly, a large amount of the fluidizer is required and a filling rate of the toner into a toner bottle is low, becoming an obstacle factor to downsizing.

[0006]

Further, a transfer process of an image formed of multiple toner to make a full-color image from a photoconductor to a transfer medium or paper is becoming more complicated. Consequently, due to poor transferability of pulverized toner, and so forth, having an amorphous shape, there is a problem such as a hollow defect in the transferred image or a large amount of toner for filling the hollow defect is consumed.

Accordingly, demands for a high-quality image without a hollow defect and for lowering running cost by further improving transfer efficiency and reducing the amount of toner consumption are increasing. If the transfer efficiency is very good, a cleaning unit for removing untransferred toner from the photoconductor or the transfer medium may not be required. This is because that an apparatus may be downsized and cost of the apparatus may be lowered. At the same time, there is an advantage that waste toner is reduced. To redeem a fault in the amorphous shape, various kinds of methods for producing spherical toner are invented.

[0007]

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In the past, many studies are conducted to improve a toner characteristic. It is known that a releasing agent (wax) having a low softening point such as polyolefin is added in toner to improve fixing performance at low temperature and offset resistance. For instance, patent documents 1 through 3 propose toner including wax having a certain endothermic peak by DSC (differential scanning calorimetry). However, the fixing characteristic at low temperature and the offset resistance of the toner are required to be further improved. In addition, it is necessary to improve developability.

[8000]

In addition, patent documents 4 through 7 propose to use candelilla wax, higher fatty acid wax, higher alcohol wax, vegetable wax (carnauba, rice), montan ester wax, and so forth, as the releasing agent. However, the fixing characteristic at low temperature and the off set resistance of the toner are required to be further improved. In addition, it is necessary to improve the developability (charging characteristic) and durability of the toner. Generally, if the releasing agent having a low softening point as described above is added in the toner, fluidity of the toner decreases, resulting in lowering the developability and the transferability. In addition, the charging characteristic, the

durability, and the storage stability are likely to be negatively affected.

[0009]

Patent documents 8 through 13 propose toner including two or more kinds of releasing agents to enlarge a fixing area (non offset area). However, the toner still has a problem in uniform dispersion of the releasing agent in the toner particles.

[0010]

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In addition, a patent document 14 proposes toner including a polyester resin and two types of offset inhibitors each having different acid values and softening points. However, the toner still has a problem in the developability. In addition, patent documents 15 and 16 specify a dispersion diameter of wax within the toner. However, since a condition and a position inside the toner are not defined, there is a case that sufficient releasing characteristic in fixing may not be obtained.

[0011]

Further, a patent document 17 proposes toner in which a spherical wax particle is fixed on a surface of the toner. However, the wax existing on the toner surface decreases fluidity of the toner, lowering the developability and the transferability. In addition, the charging characteristic, the durability, and the storage stability are likely to be negatively affected. In addition, a patent document 18 proposes a toner in which wax is included in a toner particle and the wax is locally located adjacent to a surface of the toner particle. However, there is a case that all of the offset resistance, the storage stability, and the durability are insufficient.

[0012]

At the same time, toner is generally manufactured by a kneading and pulverization method. In the method, a heat plasticity resin is melted and kneaded with a pigment and further, if needed, with a releasing agent or a charge control agent such as wax, then the

resulting mixture is finely pulverized and further graded. In some cases, if needed, an inorganic or organic fine particle may be added on a surface of the toner particle to improve fluidity or cleaning ability. In a normal kneading and pulverization method, a shape and surface structure of the toner are amorphous and subtly changes according to crushability of a material used and a condition of a pulverizing step. However, it is not easy to arbitrarily control the shape and the surface structure of the toner. In addition, it is difficult to further narrow a particle size distribution of the toner due to limiting ability in grading, and because it may increase cost. In addition, as to an average particle diameter of the particle size distribution in the toner, it is a significant task to control the average particle diameter to have a small diameter, particularly a 6 μ m or less, from a viewpoint of yield, productivity, and cost.

[0013]

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popularization along with recent years, electrophotographic technology, not only a demand for more detailed and high quality image formation, but also a demand for high-speed, reduction in size and weight, and simple handling of an apparatus, and for copying in multiple modes with a small number of sheets are arisen. Particularly, as the apparatus is increasingly used at home or personally as well as in an office, there is a demand in reduction in size and weight of the apparatus, and simplification of handling when copying a small number of sheets. In an image forming apparatus using the electrophotographic technology, charging processing, image exposure processing, and toner sequentially performed development processing are photoconductor by a charging means, an exposure means, and a development means arranged around the photoconductor. However, when the charging means performs charging, normally, development means is already raised and starts an operation required for sufficiently charging a developer, and so forth, so as to be prepared for development. A condition of the operation is maintained for a certain period for a cycle of copying which is performed later. In other words, when a relatively small number of copies such as one or a few copies are made at one copy as in a case when the apparatus is used at home or personally, toner in the developer is likely to have relatively more chances to be subjected to mechanical stress due to agitation, and so forth. In addition, a demand for a high-speed apparatus in recent years leads to rapid rise of an apparatus. This means that the toner has more chances to be subjected to severer mechanical stress due to rapid agitation in a short time, and so forth, and the toner is more likely to be subjected to intensive thermal stress in the apparatus due to the rapid rise, a high-speed operation and so forth.

[0014]

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In a case of toner formed of a binder resin and wax kneaded together, wherein the wax is included in a component of the binder resin, the wax generally exhibits poor compatibility with the binder resin. In addition, if the wax is soluble in the binder, releasing characteristic may not be developed. Thus the wax may improve its releasing characteristic only when the wax exists in the binder resin as an incompatible domain particle. As a result, the wax exists in the resin in a form of fine particle. However, the toner is likely to be grinded and have a small particle diameter by being subjected to the mechanical stress such as agitation. In addition, the toner tends to be grinded in smaller particles when the toner is subjected to intensive thermal stress such as when the toner is rapidly heated. This is because the wax and the binder resin have different coefficients of thermal expansion, and the coefficient of thermal expansion of the wax is generally 3 to 10 % higher (excluding microcrystalline wax) than the coefficient of thermal expansion of the binder resin. It is widely known that a toner particle having an excessively small particle diameter causes various kinds of inconveniences and problems.

Apart from the inconveniences and the problems, when a dry-type developer including toner is used for a long period of time, a consumption rate of toner particles forming the toner is variable. Generally, a toner particle having a large particle diameter tends to be significantly consumed than a toner particle having a small particle diameter. As a result, a composition of the toner is changed from an initial and desired composition to a composition rich in toner particles having a small diameter.

[0015]

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A technique according to the patent document 18 is excellent from a viewpoint that the patent document 18 discloses a necessity of wax being included in a toner particle and being locally existing adjacent to a surface of the particle, in order to solve a problem of thermal stability during storage of the toner caused by the wax having a low melting point existing on an outside surface of the toner particle. However, the patent document 18 neither raises an issue concerning downsizing of the toner particle in light of mechanical and thermal stress subjected to the toner during usage and undesirable relation between the resin and the wax, as described above, nor proposes a measure to solve the problem. In the technique, the wax is locally located adjacent only to the surface of the toner particle. Therefore, for instance, manufactured slurry at temperatures of 125 °C is rapidly cooled down to 25 °C within 10 seconds. Further in the technique, there is no description in the patent document as to an amount of wax with respect to a whole amount of toner. According to only embodiment in which the amount of wax is mentioned, the amount of wax with respect to the whole amount of a toner particle is less than 1 %. With the amount of wax, it is so designed that the wax does not come out and adhere to a surface of a fixing member. However, since the amount of wax is too small to exhibit releasing effect, it is easy to imagine that a margin of hot offset is not provided.

[0016]

In either case, wax included in a toner particle affects on a degree of toner fusion, fixing ability, and so forth, depending on a state of the pulverized toner particle. However, it is difficult to control pulverization of the toner particle and to control a state of the included wax in prospect of the state of the pulverized toner particle.

When the wax is uniformly dispersed in the toner particle including a vicinity of a surface of toner, an amount of wax existing on the surface of the toner is large. Accordingly, there is a problem such that the toner fuses on a carrier, and so forth. On the other hand, when the wax is not dispersed in the toner but exists only on the vicinity of the surface of toner, a part of a surface on which the wax does not exist at all becomes large. Consequently, releasing ability of the toner during development, transfer, and cleaning is varied. As a result, not only a characteristic during fixing becomes poor, but also there is also a possibility that a toner particle may easily be crushed by mechanical or thermal stress. In addition, there is also a possibility that a surface characteristic of a newly crushed fine toner particle is not desirable.

[0017]

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[Patent document 1]

Japanese Patent Application Laid-Open No. Hei6-295093

[Patent document 2]

Japanese Patent Application Laid-Open No. Hei7-84401

[Patent document 3]

Japanese Patent Application Laid-Open No. Hei9-258471

[Patent document 4]

Japanese Patent Application Laid-Open No. Hei5-341577

30 [Patent document 5]

Japanese Patent Application Laid-Open No. Hei6-123999

[Patent document 6]

Japanese Patent Application Laid-Open No. Hei6-230600

[Patent document 7] Japanese Patent Application Laid-Open No. Hei6-324514 [Patent document 8] Japanese Patent Application Laid-Open No. Heill-258934 [Patent document 9] 5 Japanese Patent Application Laid-Open No. Heill-258935 [Patent document 10] Japanese Patent Application Laid-Open No. Hei4-299357 [Patent document 11] 10 Japanese Patent Application Laid-Open No. Hei4-337737 [Patent document 12] Japanese Patent Application Laid-Open No. Hei6-208244 [Patent document 13] Japanese Patent Application Laid-Open No. Hei7-281478 15 [Patent document 14] Japanese Patent Application Laid-Open No. Hei8-166686 [Patent document 15] Japanese Patent Application Laid-Open No. Hei8-328293 [Patent document 16] Japanese Patent Application Laid-Open No. Hei10-161335 20 [Patent document 17] Japanese Patent Application Laid-Open No. 2001-305782 [Patent document 18] Japanese Patent Application Laid-Open No. 2002-6541

[Problems to be Solved]

[0018]

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It is an object of the present invention to provide toner which has improved fixing ability at low temperature and offset resistance with low electric power consumption, forms a high quality toner image, and has long-term excellent storage stability.

In addition, it is another object of the present invention to provide toner which may achieve a high quality image and has a wide fixing area. Further, it is also an object of the present invention, in a case of color toner, to provide toner excellent in glossiness and hot offset resistance.

Furthermore, it is also an object of the present invention to provide toner capable of forming a high-resolution image. It is also an object of the present invention, when the toner is used in a high-speed apparatus, to provide toner which may achieve a balance between prevention of toner fusion by running an appropriate amount of wax and an excellent fixing ability during a fixing process even when the toner is crushed by being subjected to a mechanical impact between the toner and a carrier particle, a development member, and so forth, during a development process.

Furthermore, it is also an object of the present invention to provide an image forming apparatus using the toner and a process cartridge which is attachable to or detachable from the image forming apparatus.

[0019]

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[Means for Solving the Problems]

The inventors of the present invention achieved the present invention as a result of an intensive study to develop toner having a wide fixing area, excellent particle fluidity and transferability in a case of toner having a small particle diameter, excellent heat-resistant storage stability, fixing characteristic at low temperature, and hot offset resistance. In this case, the toner is resistant to crack and a property of the toner does not change much when a toner particle cracks. Particularly, the study is done to develop dry toner which has excellent glossiness when used in a cull-color copier, and so forth, and does not require application of oil to a hear roller.

[0020]

More specifically, the problems are solved by (1) "dry toner including at least a toner binder, a colorant, and wax, characterized in that the wax is included in a toner particle in a form of fine particle and exists throughout a part adjacent to

a surface and an inner part of the toner particle, and density of the wax existing adjacent to the surface of the toner particle is greater than density of the wax existing in the inner part of the toner particle", (2) "the dry toner according to (1), characterized in that an occupied area ratio of the wax is between 5 to 40 % in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an circumference having a radius which is two-thirds of the radius of the toner particle", (3) "the dry toner according to (1) or (2), characterized in that the wax is internally included in the toner particle in a form of fine particle, and an amount of wax existing in the toner particle in the portion on the arbitral cross-section having the center of the toner particle thereon, wherein the portion is positioned between the circumference of the arbitral cross-section and the inner circumference having the radius which is two-thirds of the radius of the toner particle, is 70 % by number or more relative to the entire wax existing in the toner particle", (4) "the dry toner according to any one of (1) through (3), characterized in that the wax is not exposed on the surface of the toner particle", (5) "the dry toner according to any one of (1) through (4), characterized in that 70 % by number or more of a dispersed wax particle dispersedly existing inside the toner particle has a diameter of 0.1 to 3 μ m", (6) "the dry toner according to any one of (1) through (5), characterized in that a content of the wax in the toner is 3 to 10 parts by weight % relative to 100 parts by weight % of a component of resin", (7) "the dry toner according to any one of (1) through (6), characterized in that any one of or in combination of free fatty acid eliminated camauba wax, rice wax, montan wax, and ester wax are used as the wax", (8) "the dry toner according to any one of (1) through (7), characterized in that modified polyester (i) is included as the toner binder", (9) "the dry toner according to any one of (1) through (8), wherein

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the dry toner may be obtained by dissolving or dispersing a toner composite including the modified polyester (i) in an organic solvent, and then dispersing in an aqueous solvent", (10) "the dry toner according to any one of (1) through (9), wherein the dry toner may be obtained by generating polyester having a urea bonding of dissolving or dispersing a toner composite including a pre-polymer in the organic solvent, and then in a process of dispersing in the aqueous solvent", (11) "the dry toner according to any one of (1) through (10), characterized in that the toner binder includes unmodified polyester (LL) as well as the modified polyester (i), and that a weight ratio of the (i) to the (LL) is between 5/95 to 80/20", (12) "the dry toner according to any one of (1) through (11), characterized in that a peak molecular weight of the toner binder is 1000 to 10000", (13) "the dry toner according to any one of (1) through (12), characterized in that glass transition temperature (Tg) of the toner binder is between 40 to 70 $^{\circ}$ C", (14) "the dry toner according to any one of (1) through (13), characterized in that a volume average particle diameter (Dv) of the toner is between 3.0 to 8.0 μ m, and a ratio of the volume average particle diameter to a number average diameter (Dn), Dv/Dn, is between 1.00 to 1.20", (15) "the dry toner according to any one of (1) through (14), characterized in that an average circularity of the toner is between 0.93 to 1.00", (16) "the dry toner according to any one of (1) through (14), characterized in that a particle of the toner has a spindle shape", and (17) "the dry toner according to any one of (1) through (14) or (16), characterized in that the particle of the toner has a spindle shape, a ratio of a major axis r1 to a minor axis r2 (r2/r1) may be expressed as between 0.5 to 0.8, and a ratio of a thickness r3 to the minor axis r2 (r3/r2) may be expressed as between 0.7 to 1.0." according to the present invention.

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In addition, the problems are solved by (18) "an image forming apparatus for fixing a toner image on a transfer member by passing the transfer member between two rollers and thereby heating and

fusing the toner image, characterized in that the image forming apparatus includes a fixing device for fixing at surface pressure applied between two rollers (roller load/contact area) of 1.5 x 10^5 Pa or less", (19) the image forming apparatus according to (18), characterized in that the fixing device includes a heating member having a heat emitting member, a film contacting the heating member, and a pressing member press-contacting the heating member via the film, wherein a recording medium on which an unfixed image is formed is passed between the film and the pressing member to be fixed by heat", (20) "the image forming apparatus according to (18) or (19), characterized in that a photoconductor used for image formation is an amorphous silicon photoconductor", (21) "the image forming apparatus according to any one of (18) through (20), characterized by including a development means having an electric field printing means for applying an alternating electric field when developing a latent image on the photoconductor", and (22) "the image forming apparatus according to any one of (18) through (21), characterized by including a charging device for charging by causing a latent image carrier to contact a charging member, and applying voltage on the charging member" according to the present invention.

Further, the problem are solved by (23) "a process cartridge integrally supporting a photoconductor, and at least one means selected from a group of a charging means, development means, and a cleaning means, and is attachable to or detachable from an image forming apparatus, characterized in that the development means includes toner according to any one of (1) through (17).

[0021]

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The inventors of the present invention found toner in which a wax particle having an appropriate particle diameter is stably dispersed and a manufacturing method of the toner. In O/W type emulsion, hydrophobic wax is affected by water existing around the wax. Similarly, the wax is moved toward a hydrophobic resin. Further, the wax is penetrated into a component of the hydrophobic

binder resin which is melted and softened. It is preferred not to increase penetration speed too much (not to use a solvent having overly high solubility or not to heat too high). As a result, a penetration degree of the wax to a toner binder has some sort of grade in a direction of depth since there is a difference in number of polar group between the wax and the binder resin even though both of the wax and the resin are hydrophobic. Further, a negative adsorption occurs on a connection part of the polar group of the binder (particularly a modified polyester) at an interface of the wax. It is assumed that this leads to stable dispersion of the wax having low polarity. Further, by letting the emulsion stand for 30 to 120 minutes at 35 to 45 $^{\circ}$ C, for instance, particularly in a method of obtaining a toner particle by dissolving swelling/dispersing a toner composition in an organic solvent, and dispersing the toner particle in an aqueous solvent, the connection part having a high polarity slightly exhibits hydrophilicity. However, an effect such that a wax particle is prevented from being exposed to a surface is achieved.

[0022]

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When the wax exists from a vicinity of the toner particle surface to an interior portion of the toner particle, and a density of the wax existing around the vicinity of the toner particle surface is greater than a density of the wax existing in the interior portion of the toner particle, the wax may come out sufficiently during fixing. As a result, fixing not requiring fixing oil, what is called oilless fixing, may be achieved particularly in glossy color toner. On the other hand, even when a large amount of wax exists in a part adjacent to a center of the toner particle, it is difficult to cause the wax to come out sufficiently during fixing, which is demonstrated by an observation which is described as follows. The inventors of the present invention observed a cross-section surface of toner and transfer paper after fixing, and confirmed as a result that the wax remains in the toner particle. Further, since an amount

of wax existing on the surface of the toner particle is small under a normal usage condition, the toner has excellent durability, stability, and storage stability.

In addition, such a tendency is more significant when an occupied area ratio of the wax is between 5 to 40 % in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particle, and particularly when an amount of wax existing adjacent to the surface of the toner particle is 70 % by number or more relative to the entire wax existing in the toner particle.

[0023]

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In the wax existing in the vicinity of the surface to the inner part of the toner particle, when the density of the wax existing in the vicinity of the surface of the toner particle is lower than the density of the wax existing in the inner part of the toner particle, and particularly when an occupied area ratio of the wax is less than 5 % in the portion on the arbitral cross-section having the center of the toner particle thereon, wherein the portion is positioned between the circumference of the arbitral cross-section and the inner circumference having the radius which is two-thirds of the radius of the toner particle, it is difficult to cause the wax to come out from the surface of the toner particle during fixing even when a large amount of wax exists in the inner part of the toner particle. As a result, hot offset resistance becomes insufficient in such a case. In addition, when the occupied area ratio of the wax is more than 40%, the wax easily comes out from the surface of the toner particle, resulting in insufficient thermal resistance and durability.

30 [0024]

By dispersing wax particles of 70 % by number or more relative to a whole amount of wax in the vicinity of the surface of the toner, it is possible to cause the wax to surely and sufficiently come out during fixing. Accordingly, oilless fixing may be performed satisfactory.

[0025]

Further, distribution of a particle diameter of the dispersed wax existing in the toner particle according to the present invention is that 70 % by number or more of the wax particles have a diameter of 0.1 to 3 μ m, and preferably that 70 % by number or more of the wax particles have a diameter of 1 to 2 μ m. When a large number of wax particles have a diameter of less than 0.1 μ m, it is difficult to cause the wax to come out from the surface of the toner particle during fixing. As a result, a releasing characteristic may not be sufficiently achieved. In addition, when a large number of wax particles have a diameter of more than 3 μ m, the wax easily comes out from the surface of the toner particle, causing aggregation of toner particles. As a result, fluidity is lowered and filming may occurs. Further, in a case of color toner, color reproducibility and glossiness are significantly impaired.

[0026]

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In the present invention, a diameter of the dispersed wax particle is defined as a largest diameter of the dispersed wax particle. The diameter of the dispersed wax is measured as follows. Specifically, the toner particle is embedded in an epoxy resin and is then ultra-thinly sliced. The toner particle is dyed with ruthenium tetroxide. Thereafter, a cross-section surface of the ultra-thinly sliced toner is observed under a transmission electron microscope (TEM) at a magnification of 10000, and photographs of the toner are taken. Twenty pictures (20 particles of the toner) are subjected to image evaluation. Thus a condition of dispersed wax is observed and the diameter of the dispersed wax is measures.

[0027]

An occupied area ratio of the wax in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between the circumference of the arbitral

cross-section and the inner circumference having the radius which is two-thirds of the radius of the toner particle is obtained by dividing an existence ratio of the wax existing in the portion on the arbitral cross-section having the center of the toner particle wherein the portion is positioned circumference of the arbitral cross-section and the inner circumference having the radius which is two-thirds of the radius of the toner particle, by the area of the cross-section. The wax not existing on the toner surface but existing adjacent to the toner surface is defined, from the pictures taken as described above, as the toner existing more toward the surface of the toner than toward a curved line connecting the surface of the toner particle and a middle portion of the radius (middle point on bisected radius) (however, when wax exists on a curved line formed of the surface of the toner particle and a middle portion of the radius the wax is determined to exist on a centric portion).

[0028]

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Density of the wax existing in the vicinity of the surface of the toner particle and in the inner part of the toner particle may be directly measured by using a publicly-known measuring method. In the present invention, however, a ratio of the wax existing in the vicinity of the surface of the toner particle and the ratio of the toner existing in the inner part of the toner particle are measured by the occupied area ratio of the wax on a cross-section surface of the toner particle, which is a much simpler method compared to any publicly-known method.

Further, in the present invention, a portion adjacent to the surface of the toner particle indicates a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particle, and the inside the toner particle indicates a portion formed on an arbitral

cross-section having a center of the toner particle thereon, wherein the portion is positioned between an inner circumference having a radius which is two-thirds of the radius of the toner particle.

[0029]

In the present invention, a content of the wax in the toner is preferably 3 to 10 parts by weight % relative to 100 parts by weight % of a component of a resin. When the content of the wax relative to a whole mount of the toner is less than 3 %, it is so designed that the wax does not come out and adhere to a surface of a fixing member. However, since the amount of wax is too small to exhibit releasing effect, a margin of hot offset sometimes may not be provided. On the other hand, when the content of the wax in the toner is more than 10 % relative to 100 parts by weight of the component of resin, the wax is easily affected by a thermal energy and a mechanical energy since the wax melts at low temperature. Therefore, the wax is sometimes released from the surface of the toner particle when the toner and a carrier are agitated in a development part. Consequently, the wax adheres on a surface of the carrier, resulting in lowering a charging ability of the carrier.

[0030]

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Further, an endothermic peak of the wax measured by a differential scanning calorimeter (DSC) when temperature is increasing may be between 65 to 115 $^{\circ}$ C in terms of fixing of toner at low temperature. However, when a melting point of the wax is lower than 65 $^{\circ}$ C, fluidity of the toner tends to be poor. When the melting point of the wax is higher than 115 $^{\circ}$ C, fixing ability of the toner tends to be poor.

An object is achieved when the wax immediately comes out on the surface of the toner particle during fixing. Wax having a high acid value lowers its function as a releasing agent. To secure the function as the releasing agent, the wax is preferably free fatty acid eliminated carnauba wax, rice wax, montan wax, or ester wax each having an acid value of 5 KOHmg/g or less.

[0031]

Modified polyester in the present invention refers to a polyester resin having a bonding other than an ester bonding in the polyester, or a polyester resin having a structurally different resin component in the polyester with a covalent bonding, an ionic bonding, and so forth. The example of the modified polyester includes polyester of which terminal is reacted with other than an ester bonding. Specifically, the polyester in which a functional group capable of reacting with an acid radical and a hydroxyl group, for example an isocyanate group, and so forth, is introduced to the terminal of the polyester and thereafter the terminal are further reacted with an active hydrogen compound so as to modify the terminal of the polyester.

[0032]

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A favorable example of the modified polyester used in the present invention (i) is a reactant of a polyester pre-polymer having an isocyanate group (A) and amines (B), and so forth. Examples of the polyester pre-polymer having the isocyanate group (A) may include a reactant that is a polycondensation product of polyol (1) and poly carboxylic acid (2), and also a reactant of the polyester having an active hydrogen compound and polyisocyanate (3). Examples of the active hydrogen contained in the polyester may include a hydroxyl group (an alcoholic hydroxyl group and a phenolic hydroxyl group), an amino group, a carboxy group, a mercapto group, and so forth. Of these, the alcoholic hydroxyl group is preferable.

[0033]

Examples of the polyol (1) include diol (1-1) and polyol having 3 or more valences (1-2). They are suitably used singly or in combination of the diol (1-1) and a small amount of the polyol (1-2). Examples of the diol (1-1) may include alkylene glycol (ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butane diol, 1,6-hexane diol, and so forth), alkylene ether glycol (diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, poly tetramethylene

ether glycol, and so forth), alicyclic diol (1,4-cyclohexane dimethanol, hydrogenated bisphenol A, and so forth), bisphenols (bisphenol A, bisphenol F, bisphenol S, and so forth), an adduct of the alicyclic diol with alkylene oxide (ethylene oxide, propylene oxide, butylene oxide, and so forth) an adduct of the bisphenols with alkylene oxide (ethylene oxide, propylene oxide, butylene oxide, and so forth). Of these, the alkylene glycol having carbon atoms of between 2 to 12 and the adduct of the bisphenols with the alkylene oxide are preferable. A combination of the adduct of the bisphenols with the alkylene oxide and the alkylene glycol having carbon atoms of between 2 to 12 is particularly preferable. Examples of the polyol having 3 or more valences (1-2) may include polyhydric aliphatic alcohol having 3 to 8 valences or more (glycerine, trimethylolethane, trimethylolpropane, pentaerythritol, sorbitol, and so forth), phenols having 3 or more valences (trisphenol PA, phenol novolak, cresol novolak, and so forth), and an adduct of the polyphenol having 3 or more valences with alkylene oxide.

[0034]

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Examples of polycarboxylic acid (2) may include dicarboxylic acid (2-1) and polycarboxylic acid having 3 or more valences (2-2). The dicarboxylic acid (2-1) may suitably be used singly or in a combination with a small amount of the polycarboxylic acid (2-2). Examples of the dicarboxylic acid (2-1) may include alkylene dicarboxylic acid (succinic acid, adipic acid, sebacic acid, and so forth), alkenylene dicarboxylic acid (maleic acid, fumaric acid, and so forth), and aromatic dicarboxylic acid (phthalic acid, isophthalic acid, terephthalic acid, naphthalene dicarboxylic acid, and so forth). Of these, the alkenylene carboxylic acid having carbon atoms of between 4 to 20 and the aromatic dicarboxylic acid having carbon atoms of between 8 to 20 are preferable. Examples of the polycarboxylic acid having 3 or more valences (2-2) may include aromatic polycarboxylic acid having carbon atoms of between

9 to 20 (trimellitic acid, pyromellitic acid, and so forth). As the polycarboxylic acid (2), furthermore, acid anhydrate of the above listed examples or lower alkyl ester (methyl ester, ethyl ester, isopropyl ester, and so forth) may be used to react with the polyol (1).

[0035]

A ratio of hte polyol (1) to the polycarboxylic acid (2) is, in terms of equivalent ratio of hydroxyl group [OH] to carboxyl group [COOH] ([OH] / [COOH]), generally about 2/1 to about 1/1, preferably 1.5/1 to 1/1, and more preferably 1.3/1 to 1.02/1.

[0036]

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Examples of the polyisocyanate (3) may include aliphatic (tetramethylene diisocyanate, polyisocyanate hexamethylene diisocyanate, 2,6-diisocyanate methylcaproate, and so forth), alicyclic polyisocyanate (isophorone diisocyanate, cycrohexylmethane diisocyanate, and so forth), diisocyanate (tolylene diisocyanate, diphenylmethane diisocyanate, and so forth), aromatic aliphatic diisocyanate (α , α , α' , α' tetramethylxylene diisocyanate, and so forth), isocyanurates; a block-compound in which the polyisocyanate is blocked with phenol derivatives, oxime, caprolactom, and so forth; and a combination of two or more of the above ingredients.

[0037]

A ratio of the polyisocyanate (3) is, in terms of equivalent ratio of isocyanate group [NCO] to hydroxyl group [OH] ([NCO]/[OH]), generally about 5/1 to about 1/1, preferably 4/1 to 1.2/1, and more preferably 2.5/1 to 1.5/1. When the ratio [NCO]/ [OH] is more than 5, fixing ability at low temperature is impaired. When a mole ratio of [NCO] is less than 1, the urea content in the modified polyester becomes low hence hot offset resistance is impaired. In the pre-polymer having an isocyanate group at the terminal thereof (A), a content of polyisocyanate (3) composition is generally about between 0.5 to about 40 % by weight, preferably 1 to 30 % by weight,

and more preferably between 2 to 20 % by weight. When the content of the polyisocyanate (3) composition is less than 0.5 % by weight, not only impairing hot offset resistance, but it is disadvantageous in terms of having heat-resistant storability together with fixing ability at low temperature. When the content is more than about 40 % by weight, on the other hand, the fixing ability at low temperature is impaired.

[8800]

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A number of isocyanate groups contained in the pre-polymer having the isocyanate group (A) per molecular is generally one or more, preferably between 1.5 to 3 in average, and more preferably between 1.8 to 2.5 in average. When the number of isocyanate group per molecular is less than one, the molecular weight of urea-modified polyester becomes low, and therefore, hot offset resistance is impaired.

[0039]

Examples of the amines (B) may include diamine (B1), polyamine having 3 or more valences (B2), amino alcohol (B3), amino mercaptan (B4), amino acid (B5), and a block compound in which the amino group of (B1) to (B5) is blocked (B6). Examples of the diamine (B1) may include aromatic diamine (phenylene diamine, diethyltoluene diamine, 4,4'-diaminophenylmethane, and so forth), alicyclic diamine (4,4'-diamino-3,3'-dimethyldicycrohexylmethane, diamine cyclohexane, isophorone diamine, and so forth), and aliphatic diamine (ethylene diamine, tetramethylene diamine, hexamethylene diamine, and so forth). Examples of the polyamine having 3 or more valences may include ethylene triamine, triethylene tetramine. Examples of the amino alcohol (B3) may include ethanolamine, hydroxyethylaniline, and so forth. Examples of the amino mercaptan (B4) may include aminomethylmercaptan, aminopropylmercaptan, and so forth. Examples of amino acid (B5) may include amino propionic acid, amino capric acid, and so forth. Examples of the block compound in which the amino group of (B1) to (B5) is blocked (B6)

may include a ketimine compound, an oxazoline compound, and so forth obtained from the amines and ketones of (B1) to (B5) (acetone, methylethylketone, methylbutylketone, and so forth. Of the amines (B) listed above, the diamine (B1) and a combination of the diamine (B1) and a small amount of polyamine (B2) are preferable.

[0040]

Further, the molecular weight of the urea-modified polyester may be adjusted by using an elongation inhibitor, if needed. The elongation inhibitor may include monoamine (diethyl amine, dibutyl amine, butyl amine, lauryl amine, and so forth) and a block compound, and so forth, in which the monoamine is blocked (ketimine compound).

[0041]

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The ratio of the amines (B) is, in terms of equivalent ratio of isocyanate group [NCO] in the pre-polymer having an isocyanate group (A) to amino group [NHx] in the amines (B) ([NCO]/[NHx]), generally between 1/2 to 2/1, preferably between 1.5/1 to 1/1.5, and more preferably between 1.2/1 to 1/1.2. When the equivalent ratio [NCO]/ [NHx] is more than 2 or less than 1/2, the molecular weight of the urea-modified polyester becomes low, therefore, the hot offset the present invention, resistance is impaired. In urea-modified polyester (i) may contain urethane bondings together with urea bondings. The mole ratio of an urea bonding content to an urethane bonding content is generally 100/0 to 10/90, preferably 80/20 to 20/80, and more preferably between 60/40 to 30/70. When the mole ratio of the urea bonding content is less than 10, the hot offset resistance is impaired.

[0042]

The urea-modified polyester (u) used in the present invention is manufactured by a one-shot method or a pre-polymer method. The weight average molecular weight of the urea-modified polyester (u) is generally 10,000 or more, preferably between 20,000 to 10,000,000, and more preferably between 30,000 to 1,000,000. When the above range is attained, the peak molecular weight of the urea-modified

polyester (u) is between 1,000 to 10,000. When the peak molecular weight is less than 1,000, an elongation reaction does not easily occur and elasticity of the toner is low, consequently, the hot offset resistance is impaired. When the peak molecular weight is more than 10,000, the fixing ability is impaired and problems related to manufacturing may occur in formation of particles or pulverization, for instance. The number average molecular weight of the urea-modified polyester is not particularly limited, especially when unmodified polyester (LL) is used in combination with the urea-modified polyester as described later, and any number average molecular weight may be used to obtain the above-mentioned range of the weight average molecular weight. In a case of the urea-modified polyester (u) is used singly, the number average molecular weight is generally 20,000 or less, preferably 1,000 to 10,000, and more preferably 2,000 to 8,000. When the number average molecular weight is more than 20,000, fixing ability at low temperature and glossiness of toner used for a full-color apparatus are impaired.

[0043]

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In the present invention, not only singly, but the polyester modified by a urea bonding (u) is used in combination with an unmodified polyester (LL) as a toner binder resin. It is more preferable to use the urea-modified polyester together with the unmodified polyester (LL) than to use the urea-modified polyester singly. This is because when the unmodified polyester is used, the fixing ability at low temperature and the glossiness of the toner when the toner is used in the full-color apparatus are improved. Examples of the unmodified polyester (LL) may include a polycondensation product of the polyol (1) and the polycarboxylic acid (2) having an identical polyester composition of the urea-modified polyester (u), just as similar to the favorable urea-modified polyester (u). In addition, the unmodified polyester (LL) may also be polyester which is modified by a chemical

bonding other than an urea bonding, for instance, the polyester may be modified with an urethane bonding. It is preferable that at least a part of the (u) and the (LL) is compatible from a viewpoint of the low temperature fixing ability and the hot offset resistance. Accordingly, it is preferred that the (LL) has a similar component to the polyester component of the (u). The weight ratio of the (u) to the (LL), when the (LL) is contained together with the (u), generally 5/95 to 80/20, is preferably 5/95 to 30/70, and more preferably 7/93 to 20/80. When the weight ratio of the (u) to the (LL) is less than 5%, not only the hot offset resistance is impared, but also it is difficult to obtain heat-resistant storability together with low temperature fixing ability.

[0044]

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The peak molecular weight of the (LL) is generally between 1,000 to 10,000, preferably between 2,000 to 8,000, and more preferably between 2,000 to 5,000. When the peak molecular weight of the (LL) is less than 1,000, heat-resistant storage stability is impaired. When the peak molecular weight of the (LL) is more than 10,000, low temperature fixing ability is impaired. The hydroxyl value of the (LL) is preferably between 5 or more, more preferably between 10 to 120, and further preferably between 20 to 80. When the hydroxyl value the modified polyester is less than 5, it is difficult to obtain heat resistance storage stability together with fixing ability at low temperature. The acid value of the (LL) is between 1 to 5, and preferably between 2 to 4. Since the wax having a high acid value is used as wax, it is preferable to use a resin having a low acid value as a binder since the binder may lead to charging or high volume resistivity. Thus the toner formed from such wax and binder is suitable for a two-component toner.

30 [0045]

A glass transition point (Tg) of the toner binder used in the present invention is generally 50 $^{\circ}$ C to 70 $^{\circ}$ C, and preferably 55 $^{\circ}$ C to 65 $^{\circ}$ C. When the glass transition point (Tg) of the toner binder

is less than 50 $^{\circ}$ C, heat resistant storage stability is impaired. When the glass transition point (Tg) of the toner binder is more than 70 $^{\circ}$ C, low temperature fixing ability becomes insufficient. By containing the urea-modified polyester resin, the toner according to the present invention exhibits excellent heat-resistant storage stability, even when the glass transition point of the toner binder is low, with comparison to publicly-known polyester toner.

[0046]

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As a colorant used in the present invention, any publicly-known dyes and pigments may be used. For instance, carbon black, nigrosine dyes, black iron oxide, Naphthol Yellow S, Hansa Yellow (10G, 5G, G), cadmium yellow, yellow iron oxide, yellow ochre, chrome yellow, Titan Yellow, Polyazo Yellow, Oil Yellow, Hansa Yellow (GR, A, RN, R), Pigment Yellow L, Benzidine Yellow (G, GR), Permanent Yellow (NCG), Vulcan Fast Yellow (5G, R), Tartrazine Lake, Quinoline Yellow Lake, anthracene yellow BGL, isoindolinone yellow, red oxide, red lead oxide, red lead, cadmium red, cadmium mercury red, antimony red, Permanent Red 4R, Para Red, Fire Red, parachlororthonitroaniline red, Lithol Fast Scarlet G, Brilliant Fast Scarlet, Brilliant Carmine BS, Permanent Red (F2R, F4R, FRL, FRLL, F4RH), Fast Scarlet VD, Vulcan Fast Rubine B, Brilliant Scarlet G, Lithol Rubine GX, Permanent Red F5R, Brilliant Carmine 6B, Pigment Scarlet 3B, Bordeaux 5B, Toluidine Maroon, Permanent Bordeaux F2K, Helio Bordeaux BL, Bordeaux 10B, BON Maroon Light, BON Maroon Medium, eosine lake, Rhodamine Lake B, Rhodamine Lake Y, Alizarine Lake, Thioindigo Red B, Thioindigo Maroon, Oil Red, quinacridone red, Pyrazolone Red, Polyazo Red, Chrome Vermilion, Benzidine Orange, Perynone Orange, Oil Orange, cobalt blue, cerulean blue, Alkali Blue Lake, Peacock Blue Lake, Victoria Blue Lake, metal-free phthalocyanine blue, Phthalocyanine Blue, Fast Sky Blue, Indanthrene Blue (RS, BC), indigo, ultramarine blue, Prussian blue, Anthraquinone Blue, Fast Violet B, Methyl Violet Lake, cobalt violet, manganese violet, dioxazine violet, Anthraquinone Violet, chrome green, zinc green, chromium oxide, viridian, emerald green, Pigment Green B, Naphthol Green B, Green Gold, Acid Green Lake, Malachite Green Lake, Phthalocyanine Green, Anthraquinone Green, titanium oxide, zinc oxide, and lithopone, and mixtures thereof may be used. The content of the colorant is 1 to 15 % by weight, and preferably 3 to 10% by weight, relative to the total weight of the toner.

[0047]

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The colorant for use in the present invention may be used as a master batch which is combined with a resin. Such binder resin used for the manufacturing of the master batch or in kneading with the master batch may include, in addition to the above-mentioned modified and unmodified polyester resins, polymers of styrene and substituted styrenes such as polystyrene, poly-p-chlorostyrene, polyvinyl toluene, and so forth, styrene copolymers such as styrene-p-chlorostyrene copolymer, styrene-propylene copolymer, styrene-vinyltoluene copolymer, styrene-vinylnaphthalene styrene-methyl acrylate copolymer, styrene-ethyl copolymer, acrylate copolymer, styrene-butyl acrylate copolymer, styrene-octyl acrylate copolymer, styrene-methyl methacrylate copolymer, styrene-ethyl methacrylate copolymer, styrene-butyl methacrylate copolymer, styrene-methyl α -chloromethacrylate copolymer, styrene-acrylonitrile copolymer, styrene-vinyl methyl ketone copolymer, styrene-butadiene copolymer, styrene-isoprene styrene-acrylonitrile-indene copolymer, copolymer, styrene-maleic acid copolymer, styrene-maleic ester copolymer, and forth, polymethyl methacrylate, polybutyl methacrylate, polyvinyl chloride, acetate, polyethylenes, polyvinyl polypropylenes, polyesters, epoxy resins, epoxy polyol resins, polyurethanes, polyamides, polyvinyl butyral, polyacrylic acid resin, rosin, modified rosin, terpene resins, aliphatic or alicyclic hydrocarbon resins, aromatic petroleum

chlorinated paraffin, paraffin wax, and so forth. Each of these may be used singly or in combination of two or more.

[0048]

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The master batch according to the present invention may be obtained by mixing and kneading a resin for the master batch and the colorant with high shear force. In this case, to improve interaction between the colorant and the resin, an organic solvent may be used. In addition, the master batch is preferably prepared by a flushing method. In the flushing method, water-based paste containing the colorant and water is mixed and kneaded with the resin and an organic solvent so that the colorant moves towards the resin, and that the water and a component of the organic solvent are removed. According to the method, a wet cake containing the colorant may also be preferably used as it is, that is, without drying. The materials are preferably mixed and kneaded using a triple roll mill and other high-shear dispersing devices.

[0049]

The toner according to the present invention may contain a charge control agent, if needed. As the charge-controlling agent, any publicly-known charge-controlling agent may be used. Examples may triphenylmethane dye, a include а nigrosine chromium-containing metal complex dye, a molybdic acid chelate pigment, a rhodamine dye, an alkoxyamine, a quaternary ammonium salt (including fluorine-modified quaternary ammonium salt), alkylamide, a simplex or a compound of phosphorus, a simplex or a compound of tungsten, a fluorine-containing activator, a metallic salt of salicylic acid, a metallic salt of a salicylic acid derivative, and so forth. Specific examples thereof are BONTRON 03 of a nigrosine dye, BONTRON P-51 of a quaternary ammonium salt, BONTRON S-34 of a metal containing azo dye, E-82 of an oxynaphthoic acid metal complex, E-84 salicylic acid metal complex, E-89 of a phenol condensation product (manufacture by Orient Chemical Industries, Ltd.), TP-302 and TP-415 of molybdenum complex of quaternary ammonium salt (manufactured by Hodoya Chemical Co., Ltd.), Copy Charge PSY VP2038 of a quaternary ammonium salt, Copy Blue PR of a triphenyl methane derivative, Copy Charge NEG VP2036 and Copy Charge NX VP434 of a quaternary ammonium salt (manufactured by Hoechst Japan Ltd.), LRA-901, and LR-147 of a boric complex (manufactured by Japan Carlit Co., Ltd.); copper phthalocyanine, perylene, quinacridone, azo dyes, polymeric compounds having a functional group such as a sulfonic group, a carboxyl group, a quaternary ammonium salt, and so forth.

[0050]

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An amount of the charge control agent used in the present invention is not particularly limited and may be determined according to a type of the resin, whether any additive is used according to need, and a method of manufacturing the toner including a dispersion method. Suitable amount of the charge control agent to be used is preferably between 0.1 to 10 parts by weight, and more preferably between 0.2 to 5 parts by weight, relative to 100 parts by weight of the binder resin. When the amount of the charge control agent is more than 10 parts by weight, the charging ability of the toner becomes excessively large. Consequently, the effect of the main charge control agent is impaired, electrostatic attraction between the toner and the developing roller excessively increased, fluidity of the developer is decreased, and the image density is decreased. The charge control agent and the releasing agent may be melted and kneaded together with the master batch and the resin, and may also be added when the ingredients are melted and dispersed in an organic solvent.

[0051]

As an external additive for supplementing fluidity, developability, and a charging characteristic of a color particle achieved in the present invention, an inorganic fine particle may be preferably used. A primary particle diameter of the inorganic particle is preferably between 5 to 2 μ m, and more preferably

between 5 to 500 m μ . The specific surface the inorganic particle in terms of BET method is preferably between 20 to 500 m 2 / g. The content of the inorganic particle is preferably between 0.01 to 5% by weight, and more preferably between 0.01 to 2.0% by weight, relative to the total weight of the toner. Specific examples of the inorganic toner may include silica, aluminum, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, quartz sand, clay, mica, wollastonite, diatomaceous earth, chromium oxide, cerium oxide, red iron oxide, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium carbonate, silicon carbide, silicon nitride, and the like.

[0052]

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Another examples of the external additive may include polymeric particles such as polystyrene formed of soap-free emulsion polymerization, suspension polymerization, and dispersion polymerization; copolymers of methacrylic ester and acrylic ester; polycondensation thermosetting resins such as silicone, benzoguanamine, and nylon.

20 [0053]

A surface treatment may be suitably performed on such a plasticizer to improve hydrophobicity and to prevent deteriorating fluidity and charging characteristic even in a high humidity environment. Favorable surface treatment agents are may include a silane coupling agent, a silylation reagent, a silane coupling agent having an alkyl fluoride group, an organic titanate coupling agent, an aluminium coupling agent, silicone oil, modified silicone oil, and so forth.

[0054]

A cleaning agent for removing a developer remained a photoconductor or on a primary transfer medium after transfer may include, for instance, zinc stearate, calcium stearate, fatty acid metal salt such as stearic acid, polymeric particles formed of

soap-free emulsion polymerization such as a polymethyl methacrylate particle, a polystyrene particle, and so forth. The polymeric particles preferably have a relatively narrow particle diameter distribution and a volume average particle diameter of 0.01 to 1 $\mu\,\mathrm{m}$.

[0055]

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A production method of dry r according to the present invention is described in detail as follows.

A toner binder may be manufactured according to a following method, for instance.

Polyol (1) and polycarboxylic acid (2) are heated at temperature between 150 to 280 $^{\circ}\mathrm{C}$ under the presence of a publicly-known esterification catalyst such as tetrabuthoxytitanate, dibutyl tinoxide, and so forth. Thereafter, the mixture is decompressed, if needed, while generated water in a course of decompressing is removed, so as to yield polyester having a hydroxyl group. Then the obtained polyester having a hydroxyl group is reacted with polyisocyanate (3) at temperature between 40 to 140 $^{\circ}\mathrm{C}$ so as to yield a pre-polymer having an isocyanate group (A). Further, (A) is reacted with (B) at temperature between 0 to 140 $^{\circ}{\text{C}}$ so as to yield polyester modified with a urea bonding. When (3) is reacted, and when (A) is reacted with (B), a solvent may be used, if needed. Usable solvents are, for instance, solvents which are inactive with the isocyanate (3), such as aromatic solvents (toluene, xylene, methylethylketone, forth), ketones (acetone, methylisobutylketone, and so forth), esters (ethyl acetate, and so forth), amides (dimethylformamide, dimethylacetoamide, and so forth), and ethers (tetrahydrofuran, and so forth). In a case that the polyester unmodified with an urea bonding (LL) is used in a combination with the urea-modified polyester (u), (LL) is produced in a same manner as the polyester having a hydroxyl group, and then (LL) is dissolved and mixed into a solution after the completion of the reaction of (u).

The dry toner may be manufactured by a following method but is not to be considered limited thereto.

[0056]

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When preparing a developer, the above-mentioned inorganic particles such as a hydrophobic silica particle may be added in order to improve fluidity, storage stability, developability, and transferring ability of the developer. The external additive is mixed by using a regular powder mixer. However, it is preferable to use the mixer that equips a jacket, and so forth, and is capable of controlling interior temperature. In order to modify the negative charging state given to the external additive, it may be added in middle of the process or gradually during a process. The number of revolution, rotating speed, time and temperature may of course be changed. At first, a strong load may be given followed by a relatively weak load, or a reverse may be done.

Examples of mixing devices may include a V-shaped mixer, a rocking mixer, a Redige mixer, a Nauta mixer, a Henschel mixer, and so forth. [0057]

The toner according to the present invention may be produced by dissolving or dispersing a component of the toner to an organic solvent and dispersing the solvent to an aqueous medium. As the aqueous medium in the present invention, water is used singly, or in combination with a solvent mixable with water. Examples of the solvent mixable with water may include alcohols (methanol, isopropanol, ethylene glycol, and so forth), dimethyl formamide, tetrahydrofuran, cellosolves (methylcellosolve, and so forth), lower ketones (acetone, methylethylketone, and so forth).

[0058]

To obtain a toner particle, dispersion formed of pre-polymer having an isocyanate group (A) may be reacted with (B) in an aqueous medium, or already produced urea-modified polyester (u) may be used. As a method of stably forming dispersion formed of the urea-modified polyester (u) or the pre-polymer (A) in an aqueous medium, a method

of adding a component of a toner material such as the urea-modified polyester (u) or the pre-polymer (A) in the aqueous medium, and dispersing the urea-modified polyester (u) or pre-polymer (A) using shear force may be included. The pre-polymer (A) and other toner components such as a colorant, a colorant master batch, a releasing agent, a charge control agent, an unmodified polyester resin (hereinafter referred to a toner raw material), may be mixed together when the dispersion is formed in an aqueous medium. However, it is more preferable that the toner raw materials are mixed together, followed by adding the mixture of the toner raw materials to the aqueous medium so as to disperse. Moreover, other toner components such as the colorant, the releasing agent, the charge control agent, and so forth, are not necessarily to be mixed when forming the particle in an aqueous medium, but may be added to the particle after the particle is formed. For example, the particle is formed without including a colorant, and then the colorant is added by a conventional dyeing method.

[0059]

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The method of dispersing is not particularly limited, but conventional apparatuses of low-speed shearing, high-speed shearing, frictioninig, high pressure jet, ultrasonic wave, and so forth, may be used. Of these, the high-speed shearing apparatus is preferable in order to control a particle diameter of dispersion in a range of between 2 m to 20 μ m. There is no limitation on a number of rotation when the high-speed shearing apparatus is used, but the number of rotation is generally between 1,000 to 30,000 rpm, and preferably between 5,000 to 20,000 rpm. Dispersion time is, when a batch mixer is used, generally between 0.1 to 5 minutes, though it is not limited thereto. Temperature during dispersing is generally between 0 to 150 $^{\circ}\mathrm{C}$ (under pressure), and preferably between 40 to 98 $^{\circ}\mathrm{C}$. High temperature is more preferable from viewpoints of low viscosity of dispersion formed of the urea-modified polyester (u) or the pre-polymer (A), and

dispersibility.

[0060]

An usage amount of the aqueous medium is generally between 50 to about 20,000 parts by weight, and preferably between 100 to 1,000 parts by weight, relative to 100 parts by weight of the toner composition including the urea-modified polyester (u) or the pre-polymer (A). When the usage amount is less than 50 parts by weight, the dispersibility of the toner composition is poor and a toner particle with a predetermined particle diameter may not be achieved. When the usage amount is more than 20,000 parts by weight, it is not economical. A dispersing agent may also be used, if needed. It is preferable to use the dispersing agent from a viewpoint of a sharp particle diameter distribution and stability of dispersion.

[0061]

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An oil phase, in which the toner composition is dispersed, is emulsified and dispersed in a liquid containing water by using a dispersing agent. Examples of such dispersing agent may include anion surfactants such as alkylbenzene sulfonate, lpha -olefin sulfonate, and phosphoric ester; cationic surfactants including amine salt surfactants such as alkylamine salt, amino alcohol fatty acid derivatives, polyamine fatty acid derivatives, and imidazolin; surfactants including quaternary ammonium salt cationic surfactants such as alkyltrimethyl ammonium salt, dialkyldimethyl ammonium salt, alkyldimethylbenzyl ammonium salt, pyridinium salt, alkyl isoquinolinium salt, benzenthonium chloride; nonionic surfactants such as fatty acid amide derivatives and polyhydric alcohol derivatives; and amphoteric surfactants such as alanine, dodecyl (aminoethyl) glycine, di (octylaminoethyl) glycine, N-alkyl-N, N-dimethylammoniumbetaine, and so forth.

[0062]

Moreover, a surfactant having a fluoroalkyl group is preferable in that an effect thereof may be attained with only a little usage

amount. Examples of suitable anionic surfactant having the fluoroalkyl group may include fluoroalkyl carboxylic acid having carbon atoms of between 2 to 10 and metal salts thereof, disodium perfluorooctane sulfonylglutamate, sodium 3 - [omega - fluoroalkyl (C6 - C11) oxy] - 1 - alkyl (C3 - C4) sulfonate, sodium 3 - [omega - fluoroalkyl (C6 - C8) - N - ethylamino] - 1 - propane sulfonate, fluoroalkyl (C11 - C20) carboxylic acid and metal salts thereof, perfluoroalkyl carboxylic acid (C7 - C13) and metal salts thereof, perfluoroalkyl (C4 - C12) sulfonate and metal salts thereof, perfluorooctanesulfonic acid dietanolamide, N - propyl - N - 2 - hydroxyethyl perfluorioctane sulfonamide, perfluoroalkyl (C6 - C10) sulfonamide propyltrimethylammonium salt, perfluoroalkyl (C6 - C10) - N - ethylsulfonyl glycine salt, monoperfluoroalkyl (C6 - C16) ethylphosphate, and so forth.

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Examples of commercially available products thereof are Surflon S-111, S-112, S-113 (manufactured by Asahi Glass Co., Ltd.), Fluorad FC-93, FC-95, FC-98, FC-129 (manufactured by Sumitomo 3M Limited), UNIDAYNE DS-101, DS-102 (manufactured by Daikin Industries, Ltd.), MEGAFACE F-110, F-120, F-113, F-191, F-812, F-833 (manufactured by Dainippon Ink and Chemicals Incorporated), Ektop EF-102, 103, 104, 105, 112, 123A, 123B, 306A, 501, 201, 204 (manufactured by Tohkem Products Corporation), and Ftergent F-100, F-150 (manufactured by Neos Co., Ltd.), and so forth.

[0064]

Examples of the cationic surfactant may include primary, secondary or secondary aliphatic amines having a fluoroalkyl group, quaternary ammonium salts of fatty acids such as perfluoroalkyl (C6 to C10) sulfonamide propyltrimethylammonium salt, benzalkonium chloride, benzenthonium chloride, pyridinium salt, and imidazolinium salt. Commercially available products may include, for instance, Surflon S-121 (manufactured by Asahi Glass Co., Ltd.), Fluorad FC-135 (manufactured by Sumitomo 3M Limited), UNIDAYNE

DS-202 (manufactured by Daikin Industries, Ltd.), MEGAFACE F-150, F-824 (manufactured by Dainippon Ink and Chemicals Incorporated), and Ftergent F-300 (manufactured by Neos Co., Ltd.), and so forth. [0065]

In addition, water-insoluble inorganic compound may also be used as a dispersing agent. Examples of such compound are tricalcium phosphate, calcium carbonate, titanium oxide, colloidal silica, hydroxyapatite, and so forth.

[0066]

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In addition, polymeric protecting colloid may be used to stabilize dispersion drops. Examples of the polymeric protecting colloid may include acids such as an acrylic acid, an methacrylic acid, an α - cyanoacrylic acid, an itaconic acid, an crotonic acid, an fumaric acid, and a maleic acid; (meth) acrylic monomer having a hydroxyl group such as a beta -hydroxyethyl acrylic acid, a beta - hydroxyethyl methacrylic acid, a beta -hydroxypropyl acrylic acid, a beta -hydroxypropyl methacrylic acid, a γ - hydroxypropyl acrylic acid, a γ - hydroxypropyl methacrylic acid, a 3-chloro 2 hydroxypropyl acrylic acid, a 3 - chloro 2 - hydroxypropyl diethyleneglycol acid, monoacrylic methacrylic diethyleneglycol monomethacrylic ester, glycerin monoacrylic ester, glycerin monomethacrylic ester, N-methylolacrylamide, N-methylolmethacrylamide, and the like; vinyl alcohol or ethers with vinyl alcohol such as vinylmethylether, vinylethylether, vinylpropylether, or the like; esters of a compound having vinyl alcohol and a carboxyl group such as vinyl acetate, vinyl propionate, acrylamide, methacrylamide, and vinyl lactate; and methylol compounds thereof; diacetoneacrylamide, chlorides such as acryl chloride, methacryl chloride, or the like; homopolymers or co-polymers having a nitrogen atom or its heterocyclic ring, such as vinyl pyridine, vinyl pyrolidone, vinyl ethylene imine; polyoxyethylenes imidazole, and polyoxyethylene, polyoxypropylene, polyoxyethylene alkylamine,

polyoxypropylene alkylamine, polyoxyethylene alkylamide, polyoxypropylene alkylamide, polyoxyethylene nonylphenylether, polyoxyethylene laurylphenylether, polyoxyethylene stearic phenylester, and polyoxyethylene nonylphenylester; and celluloses such as methyl cellulose, hydroxymethyl cellulose, hydroxypropyl cellulose.

[0067]

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In order to remove an organic solvent from the obtained emulsified dispersion, the whole part thereof may be gradually heated so as to completely evaporate and remove the organic solvent in a vapor drop. It is also possible to completely remove the non-soluble organic solvent in the vapor drop by spraying the emulsified dispersion into a dry atmosphere so as to form a toner fine particle. In this case, the aqueous dispersing agent can also be evaporated and removed together with the organic solvent. Examples of the dry atmosphere are heated gases such as air, nitrogen, carbon dioxide, and combustion gas. Draft of the above-mentioned gases which is heated at higher temperature than the highest boiling point of the used solvents is generally used. A targeting quality is efficiently achieved with a high-speed treatment such as using a spray dryer, a belt dryer, and a rotary kiln.

[8800]

When a material soluble in acid such as calcium phosphate or in alkali is used a dispersing stabilizer, acid such as hydrochloric acid is applied for dissolving calcium phosphate, and so forth, and thereafter the particles are subjected to rinse with water so as to remove calcium phosphate from the particle. Further, enzymes or the like may also be used to decompose the dispersing stabilizer so as to remove the dispersing stabilizer from the particle.

[0069]

In a case that the dispersing agent is used, the dispersing agent may be left on a surface of toner particle. However, it is preferable to wash the dispersing agent off after elongation and/or

cross-linking reaction from a viewpoint of charging ability of the toner.

A solvent, which may dissolve the urea-modified polyester (u) or the (A), may also be used to lower viscosity of the toner composition. It is preferred to use the solvent in terms of sharp particle diameter distribution. Moreover, the solvent preferably has a boiling point of less than 100 $^{\circ}\mathrm{C}$ and exhibits volatility from a viewpoint of ease of elimination. Examples of the solvent are toluene, xylene, benzene, carbon tetrachloride, methylene chloride, 1, 2 - dichloroethane, 1, 1, 2 - trichloroethane, chloroform, monochlorobenzene, dichloroethylidene, methyl acetate, ethyl acetate, methylethylketone, methylisobutylketone, and so forth. These may be used singly or in combination of two or more. Of these, particularly preferable solvents are aromatic solvents such as toluene and xylene, and halogenated hydrocarbons such as methylene 2 - dichloroethane, chloroform, and carbon 1. chloride. tetrachloride. The usage amount of the solvent is generally between 0 to 300 parts by weight, preferably between 0 to 100 parts by weight, and more preferably between 25 to 70 parts by weight, relative to 100 parts by weight of the pre-polymer (A). In order to remove the solvent, the solvent is heated under normal pressure or reduced pressure after the elongation and/or the cross-linking reaction.

[0070]

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The reaction time of the elongation and/or the cross-linking reaction is selected according to the reactivity of a combination of an isocyanate group structure within the pre-polymer (A) and the amines. The reaction time is generally between 10 minutes to 40 hours, and preferably between 2 to 24 hours. The reaction temperature is generally between 0 to 150 $^{\circ}$ C, and preferably between 40 to 98 $^{\circ}$ C. Additionally, publicly-known catalysts may be used, if required. Examples of the catalyst are dibutyltin laurate, dioctyltin laulate, and so forth.

[0071]

In order to remove an organic solvent from the obtained emulsified dispersion, the whole part thereof may be gradually heated so as to completely evaporate and remove the organic solvent in a vapor It is also possible to completely remove the non-soluble organic solvent in the vapor drop by spraying the emulsified dispersion into a dry atmosphere so as to form a toner fine particle. In this case, the aqueous dispersing agent can also be evaporated and removed together with the organic solvent. Examples of the dry atmosphere are heated gases such as air, nitrogen, carbon dioxide, and combustion gas. Draft of the above-mentioned gases which is heated at higher temperature than the highest boiling point of the used solvents is generally used. A targeting quality is efficiently achieved with a high-speed treatment such as using a spray dryer, a belt dryer, and a rotary kiln. If a particle size distribution is wide at the time of emulsified dispersion, and washing and drying processing is performed while keeping the particle distribution, the particles are graded so as to achieve the desired particle size distribution.

[0072]

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The grading of particles may be carried out in the solution using a cyclone, a decanter, centrifugal, and so forth, so as to remove a fine particle part. Although the grading may be carried out on dried particles after drying, it is preferable to perform the grading in a solution from a viewpoint of efficiency of the process.

The obtained unwanted irregular particles or coarse particles may be sent back to the kneading process to be used in formation of the particles. In this case, the fine particles or the coarse particles may be in a wet condition.

The dispersing agent is preferably removed from the obtained dispersion liquid, and more preferably removed at the same time of the grading mentioned above.

[0073]

The obtained dried toner particles are mixed with other particles

such as a mold-releasing agent particle, a charge control particle, a superplasticizer particle, and a colorant particle. Thereafter, mechanical impact force is applied to the mixed particles so as to fix or fuse the particles on the surface of the toner particle. In this way, other particles may be prevented from being removed from a surface of the obtained complex particle.

[0074]

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Specific means for applying impact force are, for example, a method in which the impact force is applied to the mixed particles by using a impeller blade rotating in high speed, a method of placing the mixed particles in high-speed flow so as to cause the mixed particles or complex particles to collide with a suitable collision board. Examples of the apparatus may include an angmill (manufactured by Hosokawa Micron Corporation), a modified I-type mill (manufactured by Nippon Pneumatic MFG, Co., Ltd) of which pulverizing air pressure is reduced, a hybridization system (manufactured by Nara Machine Corporation), a Kryptron System (manufactured by Kawasaki Heavy Industries, Ltd.), an automatic mortar, and so forth.

[0075]

A volume average particle diameter (Dv) of the toner according to the present invention is between 3 to 8 μ m, and the ratio (Dv/Dn) of number average particle diameter (Dn) to the volume average particle diameter (Dv) is between 1.00 to 1.20. It is preferable that the volume average particle diameter (Dv) is between 3 to 6 μ m and the ratio Dv/Dn is between 1.00 to 1.15 from viewpoints of excellent heat resistant storage stability, low temperature fixing ability, and hot offset resistance of the dry toner. Especially glossiness of an image becomes excellent in a case that the toner is used in a full-color copier. Further, in a case that the toner is used as a two component developer, variation of the toner particle diameter is minimized even when consumption and addition of the toner is repeatedly performed in a development device for a long

period of time, and favorable and stable developability may be achieved, accordingly. In a case that the toner is used as a one component developer, not only the variation of the toner particle diameter is minimized, but also filming of the toner to a developing roller, and toner fusion of a member such as a toner blade for thinning a layer of the toner are also prevented. Hence, even when the toner is used (stirred) in the development device for a long period of time, stable and excellent developability and images may be obtained.

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It is generally said that the smaller a toner diameter is, the more advantageous to obtain higher image resolution and image quality. On the other hand, the toner having a smaller toner diameter is disadvantageous in transferability and cleaning ability. When a volume average particle diameter of the toner is smaller than the diameter according to the present invention, in a case of a two component developer, the toner is prone to fuse onto a surface of a carrier by being stirred in the development device for a long period of time, lowering charging ability of the carrier. When a single-component developer is used as the toner, toner filming to a developing roller and toner fusion to a member such as a blade for thinning a layer of the toner are likely to occur.

These phenomena are largely related to a content of fine particles. If a toner contains toner particles having a diameter of 3 μ n or less at more than 10 % by number relative to the total number thereof, the toner is more likely to adhere onto the carrier. Therefore, a problem occurs when stability of charge is highly required.

On the other hand, when a particle diameter of toner is larger than a size according to the present invention, not only it is hard to obtain an image of high resolution and high quality, but also the toner particle diameter often varies largely when the toner is consumed and supplied during developing. In addition, when the ration Dv/Dn is 1.20 or more, resolution tends to be lowered. When the toner particle diameter is 3 μ m or less, suspended toner particles may harm a human body. When the toner particle diameter is 8 μ m or more, sharpness of toner image on a photoconductor is decreased, hence an image resolution is decreased.

[0077]

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An average particle diameter and a particle size distribution of toner are measured by a coulter counter method. Measuring devices according to the coulter counter method may include a Coulter Counter TA-II and a Coulter Multisizer II (manufactured by Beckman Coulter, Inc.). In the present invention, an average particle diameter and a particle diameter distribution of a toner are measured by using the Coulter Counter TA-II connected with a personal computer PC 9801 (manufactured by NEC Corporation) in which an Inter Face (manufactured by Institute of Japanese Union of Scientists & Engineers) is installed. The Inter Face is capable of analyzing and outputting a number distribution and a volume distribution of toner.

[0078]

The circularity of the dry toner according to the present invention is measured by using a flow-type particle image analyzer FPIA-2000 (manufactured by Sysmex Corporation).

The average circularity of the dry toner according to the present invention is in a range of between 0.93 to 1.00. It is very important for the toner according to the present invention to have a certain shape and a certain distribution of the shape. When an average circularity of the toner is less than 0.93 and the shape of the toner particle is too amorphous to be a round shape, sufficient transferability or a high quality image without dust may not be obtained. The toner having amorphous shape has stronger adhesion force such as van der Waals force and image force than a relatively spherical particle because the toner has more contact points a smooth medium such as a photoconductor, and charges tend to be

concentrated in the concave portions. Accordingly, in an electrostatic transferring process, in the toner formed of a mixture of an amorphous particle and a spherical particle, the particle having a spherical shape are selectively moved, resulting in a hollow defect in a character part or a line image part.

In addition, there are also problems in that the remained toner is to be removed for a next a toner yield (a usage ratio of the toner for image formation) is low. A circularity of the pulverized toner is generally 0.910 to 0.920. Specific measuring method of the circularity is explained later.

[0079]

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When the toner according to the present invention used in a two component developer, the toner is mixed with a magnetic carrier. The toner content in the double-component developer is 1 to 10 parts by weight relative to 100 parts by weight of the magnetic carrier. The magnetic carrier may be selected from any publicly-known carriers such as an iron particle, a magnetite particle, or a magnetic resin carrier, having a particle diameter of 20 to 200 Coating materials may include an amino resin such as a urea-formaldehyde resin, a melamine resin, a benzoguanamine resin, a urea resin, a polyamide resin, an epoxy resin, and so forth. Another examples are polyvinyl or polyvinylidene resins such as polymethylmethacrylate acrylic resin, а polyacrylonitrile resin, a polyvinyl acetate resin, a polyvinyl alcohol resin, and a polyvinylbutyral resin; polystyrene resins such as a polystyrene resin and a styrene-acryl copolymer resin; halogenated olefin resins such as polyvinyl chloride or the like; polyester resins such as a polyethyleneterephthalate resin and a polybutyleneterephtalate resin; a polycarbonate polyethylene resin, a polyvinyl fluoride resin, a polyvinylidene polytrifluoroethylene fluoride resin, a polyhexafluoropropyrene resin, a copolymer of vinylidene fluoride and acryl monomer, a copolymer of vinylidene fluoride and vinyl

fluoride, fluoro terpolymers such as terpolymer tetrafluoroethylene, vinylidene fluoride, and non-fluoride like. Further, silicone resin, and the electroconductive particle, and so forth, may be added in a coating resin, if required. Examples of the electroconductive particles are metal particles, carbon black, titanium oxide, tin oxide, zinc The electroconductive particle preferably has oxide, and so forth. an average particle diameter of 1 μ m or less. If the average particle diameter is more than 1 μ m, it is hard to control electric resistance.

The toner according to the present invention may also be suitably used as one component magnetic toner or non-magnetic toner.

[0800]

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A preferable embodiment of the toner according to the present invention is further described below. The toner according to the present invention preferably has a spindle shape.

Following problems occur when the shape of the toner is irregular or compressed and the toner has poor particle fluidity because of its shape. A problem such as background soiling is likely to occur because friction charge may not be smoothly performed. In addition, when developing a fine latent image dot, it is difficult for such badly shaped toner to be precisely and uniformly placed. Therefore, such toner generally has poor dot reproducibility. Further, there is a problem in transfer efficiency in a latent electrostatic transferring method since the irregularly shaped toner may not be affected by electric line of force.

In a case that a shape of toner is close to a sphere, a particle fluidity of the toner is overly increased, hence the toner excessively reacts with external force. Consequently, a problem arises in that the toner particles are easily scattered outside the dot during developing and transferring. In addition, cleaning failures are more likely to occur since the sphere shaped toner is easily rolled out into a space between a photoconductor and a

cleaning member.

Since the toner according to the present invention has a spindle shape and particle fluidity is adequately controlled, friction charge is smoothly performed on the toner and thus a very fine dot may be orderly developed without an occurrence of background soiling, thereafter the developed toner dot image is efficiently transferred. Consequently, the toner present invention has excellent dot reproducibility. In addition, particle fluidity of the toner is appropriately controlled so that scattering of toner is prevented. The spindle shaped toner particle has a limited rolling axis compared to the spherical toner particle. Consequently, a cleaning failure such that the toner is rolled down beneath the cleaning member may not easily occur.

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As shown in a frame format in Fig. 1, toner according to the present invention is preferably in a spindle shape in which a ratio of a major axis r1 to a minor axis r2 (r2/r1) is between 0.5 to 0.8, and a ratio of a thickness r3 to the minor axis r2 (r3/r2) is between 0.7 to 1.0. In addition, as shown in a schematic cross-sectional view in Fig. 1, the toner is characterized in that a density of wax existing adjacent to a surface of the toner is denser than the wax existing inner part of the toner.

When the ratio of the major axis to the minor axis (r2/r1) is less than 0.5, a cleaning property of the toner is high because a shape of the toner particle is less spherical. However, since dot reproducibility and transfer efficiency are inferior, high quality images may not be obtained.

When the ratio of the major axis to the minor axis (r2/r1) is more than 0.8, a cleaning failure sometimes occurs specially in low temperature and low humidity environment since the toner particle shape becomes closer to sphere.

Moreover, when the ratio of the thickness to the minor axis (r3/r2) is less than 0.7, the toner particle has an almost flat

shape. Therefore, though toner scatters less compared to the amorphous toner but high transferability as in the spherical toner may not be obtained. Particularly, when the ratio of the thickness to the minor axis (r3/r2) is 1.0, a shape of the toner becomes a rotating body having the main axe as a rotating axe. By forming the shape of the toner close to a shape satisfying the ratio, the shape of the toner particle becomes other than amorphous, flat, and spherical. Accordingly, with the shape, all of friction charging ability, dot reproducibility, transfer efficiency, scattering inhibition, and cleaning ability are satisfied.

Fig. 1 is a drawing illustrating relation between a major axis, a minor axis, and a thickness of the toner particle. The major axis, the minor axis, and the thickness are indicated by r1, r2, and r3, respectively. A length of r1, r2, and r3 is monitored and measured by taking pictures from different angles using a scanning electron microscope (SEM).

[0082]

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An image forming apparatus according to the present invention uses the toner according to the present invention. The image forming apparatus fixes a toner image on a transfer material by causing the toner image pass through a nip between two rollers for heating and fusing. The image forming apparatus is characterized in that fixing is performed with a surface pressure applied between the two rollers (roller load/contact area) is 1.5 X 10⁵Pa or less.

Fig. 2 is a schematic diagram illustrating a fixing device of the image forming apparatus according to the present invention. In Fig. 2, (1), (2), (3), (4), (5), (6), (7), (8), (T), and (S) indicate a fixing roller, a pressing roller, a metal cylinder, an offset inhibiting layer, a heating lamp, a metal cylinder, an offset inhibiting layer, a heating lamp, a toner image, and a support body (transfer paper such as a sheet), respectively.

In the fixing device which may be used in the image forming apparatus according to the present invention, conventionally,

fixing is not performed with the surface pressure (roller load/contact area) applied on the nip between the two rollers of 1.5×10^5 Pa or less.

Conventionally, the surface stress is more than 1.5×10^5 Pa, otherwise fixing becomes insufficient. On contrary, the toner according to the present invention is capable of fixing at low temperature so that it is possible to perform fixing with the surface stress of 1.5×10^5 Pa or less. By performing fixing with low surface stress, a toner image is not pushed onto the recording medium and thus a high definition image may be output.

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The image forming apparatus according to the present invention is characterized in that the toner according to the present invention is used, and includes a fixing device. The fixing device includes a heating member having a heat emitting member, a film contacting the heating member, and a pressing member contacting the heating member via the film. In the fixing device, a recording medium on which an unfixed image is formed is passed through a nip between the film and the pressing member to heat and fix the image on the recording medium.

As illustrated in Fig. 3, the fixing device according to the present invention is a so-called surf fixing device. In the surf fixing device, fixing is performed by rotating a fixing film. A detailed explanation is given below. The fixing film, a heat resisting film in a form of endless belt, is suspended around a drive roller which is a supportive rotating body of the fixing film, a driven roller, and a heating member which is fixedly supported by a heater support body provided below both of the driver roller and the driven roller.

The driven roller also functions as a tension roller of the fixing film. The fixing film is driven to rotate in a clockwise direction by rotation drive of the driven roller in a clockwise direction as illustrated in the figure. Rotation speed is so controlled that

speed of a transfer material and a fixing film is equivalent at a fixing nip area L at which the pressing roller and the fixing film contact with each other.

The pressing roller has a flexibility layer having an excellent releasing characteristic such as silicone rubber. The pressing roller rotates in a counterclockwise direction, while contacting the fixing nip area L with a total contact pressure of between 4 to 10 kg.

The fixing film preferably has excellent heat resistance, releasing ability, and wearing resistance. The thickness of the fixing film is to be thin such as 100 $\mu\mathrm{m}$ or less, and preferably 40 $\mu\mathrm{m}$ or less. Examples of the fixing film are single or multi layered film of a heat resistant resin such as polyimide, polyether imide, PES (polyether sulfide), PFA (tetrafluoroethylene - perfluoroalkylvinylether copolymer), and so forth. Or may be a film having a thickness of 20 $\mu\mathrm{m}$ in which a releasing coat layer of 10 μ m thickness formed of a fluoride resin added with an electroconducting agent such as PTFE (polytetrafluoroethylene resin), PFA, and so forth, or an elastic layer such as fluorocarbon rubber, silicone rubber, and so forth, is applied on the side contacting with an image.

[0084]

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In Fig. 3, the heating member is formed of a flat board and a fixing heater. The flat board is formed of a material having high thermal conductivity and high electric resistance such as alumina. The fixing heater formed of a resistant exothermic body is arranged on a surface of the plane board contacting the fixing film in a longitudinal direction. Such fixing heater is coated with electrical resistant material such as Ag/Pd and Ta₂N in a form of line or a stripe by screen printing. In addition, an electrodes, not shown, is formed on both end portions of the fixing heater. The resistant exothermic body is heated by applying current between the electrodes. Further, a fixing thermal sensor formed of a

thermistor is provided on a surface of the plane board opposite to a surface on which the fixing heater is provided.

Thermal information of the board detected by the fixing thermal sensor is sent to a control means, not shown. Consequently, electrical energy to be supplied to the fixing heater by the control means is controlled. Thus the heat emitting member is controlled to predetermined temperature.

[0085]

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A process cartridge according to the present invention, using the toner according to the present invention, characterized in that at least one means selected from a photoconductor, a charging means, a development means, and a cleaning means is supported integrally with the process cartridge, and is attachable to/detachable from an image forming apparatus body.

Fig. 4 is a schematic diagram illustrating a configuration of the image forming apparatus having the process cartridge according to the present invention.

In the figure, reference numerals (10), (11), (12), (13), and (14) indicate a process cartridge as a whole, a photoconductor, a charging means, a development means, and a cleaning means, respectively.

In the present invention, a plurality of components among the photoconductor (11), the charging means (12), the development means (13), the cleaning means (14), and so forth, are integrally connected to form the process cartridge. The process cartridge is designed to be attachable to/detachable from the image forming apparatus such as a copier and a printer.

[0086]

In the image forming apparatus having the process cartridge according to the present invention, the photoconductor is driven to rotate at a predetermined peripheral velocity. In a rotating process, the charging means uniformly charges a circumference surface of the photoconductor at a predetermined positive or

negative potential. Then an image exposure means such as slit exposure or laser beam scanning exposure irradiates an image exposure light on the circumference surface of the photoconductor. In this way, an electrostatic latent image is sequentially formed on the circumference surface of the photoconductor. development means develops the formed electrostatic latent image with toner and a developed toner image is then sequentially transferred on a transfer material fed from a paper feeding part to a nip between the photoconductor and the transfer means in synchronization with rotation of the photoconductor. The transfer material on which the image is transferred is separated from a surface of the photoconductor and then introduced to an image fixing means to fix the image. Then the fixed image is printed out as a copying material (copy) and discharged outside the apparatus. cleaning means removes the toner remained on the surface of the photoconductor after image transfer to clean the surface of the photoconductor. Further, the surface of the photoconductor is then discharged so as to be repeatedly used for following image formation.

[0087]

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The image forming apparatus according to the present invention is characterized in that the photoconductor used for image formation is an amorphous silicon photoconductor.

(Amorphous silicon photoconductor)

In the present invention, the amorphous silicon photoconductor (hereinafter referred to as "a-Si photoconductor") may be used as an electrophotographic photoconductor. The a-Si photoconductor has a photoconductive layer formed of a-Si. The photoconductive layer is formed on a support body by a coating method such as vacuum deposition method, a spattering method, an ion plating method, a thermal CVD method, an optical CVD method, and a plasma CVD method. Of these, preferable method is the plasma CVD in which raw material gas is decomposed by glow discharge of direct current, high

frequency, or microwave, and then a-Si is deposited on the support body to form an a-Si film.

[8800]

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(Layer structure)

An example of the layer structure of the amorphous silicon photoconductor is as follows. Fig. is a schematic drawing illustrating a layer structure of the amorphous silicon photoconductor. An electrophotographic photoconductor (500) illustrated in Fig. 5(a) has a support body (501) and a photoconductive layer (502) on the support body (501). photoconductive layer (502) is formed of a-Si: H, X, and exhibits photoconductivity. An electrophotographic photoconductor (500) illustrated in Fig. 5(b) has a support body (501), and a photoconductive layer (502) and an amorphous silicon surface layer (503) on the support body (501). The photoconductive layer (502) is formed of a-Si: H, X, and exhibits photoconductivity. electrophotographic photoconductor (500) illustrated in Fig. 5(c) is formed of a support body (501), and a photoconductive layer (502), an amorphous silicon surface layer (503), and an amorphous silicon charge injection inhibiting layer (504) on the support body (501). The photoconductive layer (502) is formed of a-Si: H, X, and exhibits photoconductivity. An electrophotographic photoconductor (500) as illustrated in Fig. 5(d) has a support body (501) and a photoconductive layer (502) on the support body (501). photoconductive layer (502) is formed of an electric charge generating layer (505) formed of a-Si: H, X and an electric charge transport layer (506). An amorphous silicon surface layer is further provided on the photoconductive layer (502).

[0089]

30 (Support body)

The support body of the photoconductor may be conductive or electrically insulative.

The substrate of the photoconductor may be conductivity or isolating.

Examples of the conductive support body may include metals such as Al, Cr, Mo, Au, In, Nb, Te, V, Ti, Pt, Pd, and Fe, and alloys thereof such as stainless. In addition, an electrically insulative support body formed of a film or a sheet of a synthetic resin such as polyester, polyethylene, polycarbonate, cellulose acetate, polypropylene, polyvinyl chloride, polystyrene, and polyamide, glass and ceramic may be used. In this case, at lease a surface of the electrically insulative support body forming the photoconductive layer is to be treated to yield conductivity.

A shape of the support body may be in a form of cylinder, a plate, or en endless belt, which has a smooth or irregular surface. A thickness of the support body may appropriately be determined so as to form an intended photoconductor for the image forming apparatus. However, in a case that flexibility is required of the photoconductor for the image forming apparatus, thickness of the support body may be reduced as much as possible provided that the thickness is within a range that a function as the support body may be sufficiently achieved. However, the thickness of the support body is generally 10 $\mu\,\mathrm{m}$ or more from a view point of manufacturing, handling, mechanical strength, and so forth.

[0090]

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(Injection inhibiting layer)

In the photoconductor which may be used in the present invention, it is further effective to provide a charge injection inhibiting layer inhibiting a charge injection from a conductive support body side between the conductive support body and the photoconductive layer (refer to Fig. 5(c)). The charge injection inhibiting layer is polarity independent. In other words, when a charging process with a fixed polarity is performed on a free surface of the photoconductor, the charge injection inhibiting layer functions to inhibit the charge to be injected from the support body side to the photoconductive layer side, and when a the charging process with an opposite polarity is performed, such a function may not

be achieved. To provide such a function, a relatively large amount of atoms controlling the conductivity is included in the charge injection inhibiting layer compared to the photoconductive layer.

The thickness of the charge injection inhibiting layer is preferably between 0.1 to 5 μ m, more preferably between 0.3 to 4 μ m, and furthermore preferably between 0.5 to 3 μ m, from a viewpoint of an economic effect and that a desirable characteristic of an electrophotography may be achieved.

[0091]

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(Photoconductive layer)

The photoconductive layer is formed above the support body if needed. The thickness of the photoconductive layer is determined according to a desired value in view of an economic effect and that a desirable characteristic of an electrophotography may be achieved. The thickness of the photoconductive layer is preferably 1 to 100 μ m, more preferably between 20 to 50 μ m, and furthermore preferably between 23 to 45 μ m.

[0092]

(Electric charge transport layer)

When the function of the photoconductive layer is separated, the electric charge transport layer mainly functions to transport a charge. The electric charge transport layer includes at least a silicon atom, a carbon atom, and a fluoride atom as a constituent element. If needed, the electric charge transport layer further includes a - SiC (H,F,O) including a hydrogen atom and an oxygen atom. Such an electric charge transport layer has a desirable photoconductivity, particularly an electric charge generating characteristic, an electric charge holding characteristic, and electric charge transporting characteristic. In the present invention, it is particularly preferable that the electric charge transport layer includes the oxygen atom.

The thickness of the electric charge transport layer is determined according to a desired value in view of an economic effect

and that a desirable characteristic of an electrophotography may be achieved. The thickness of the electric charge transport layer is preferably between 5 to 50 μ m, more preferably between 10 to 40 μ m, and optimally between 20 to 30 μ m.

[0093]

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(Electric charge generating layer)

When the function of the photoconductive layer is separated, the electric charge generating layer mainly functions to generate a charge. The electric charge generating layer includes at least a silicon atom but does not substantially include a carbon atom. If needed, the electric charge generating layer further includes a - Si; H including a hydrogen atom. Such an electric charge generating layer has a desirable photoconductivity, particularly an electric charge generating characteristic and an electric charge transporting characteristic.

The thickness of the electric charge generating layer is determined according to a desired value in view of an economic effect and that a desirable characteristic of an electrophotography may be achieved. The thickness of the electric charge generating layer is preferably between 0.5 to 15 μ m, more preferably between 1 to 10 μ m, and optimally between 1 to 5 μ m.

[0094]

(Surface layer)

The amorphous silicon photoconductor which may used in the present invention may further include a surface layer above the photoconductive layer formed on the support body as describe above, if needed. In this case, the surface layer may be formed of amorphous silicon. The surface layer has a free surface in order to achieve an objective of the present invention mainly from a viewpoint of moisture resistance, repeating property, electric pressure tightness, environmental capability, and durability

The thickness of the surface layer according to the present invention is generally between 0.01 to 3 $\mu\,\mathrm{m}$, preferably between

0.05 to 2 μ m, and optimally between 0.1 to 1 μ m. When the thickness of the surface layer is less than 0.01 μ m, the surface layer is worn out during usage of the photoconductor due to wearing, and so forth. When the thickness of the surface layer is more than 3 μ m, an electrophotography property is impaired, such as an increase of residual charge, and so forth.

[0095]

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The image forming apparatus according to the present invention is characterized in that an alternating electric field is applied when a latent image on the photoconductor is developed.

In a development device according to an embodiment as illustrated in Fig. 6, a power supply (22) applies a vibration bias voltage as a development bias, in which a direct-current voltage and an alternating voltage are superposed, to a development sleeve (21) during development. An electric potential of a background part and an image part are positioned between a maximum value and a minimum value of the vibration bias potential. Consequently, the alternating electric field, in which directions alternately change, is formed in a development part (23). Toner and a carrier in a development agent intensively vibrate in the alternating electric field. As a result, the toner is scattered onto a photoconductive drum (24), shaking off the development sleeve (21) and electrostatic binding force toward the carrier. The toner is then adheres to the photoconductive drum relative to a latent image thereon.

A difference between the maximum value and the minimum value of the vibration bias voltage (voltage between peaks) is preferably between 0.5 to 5 KV, and a frequency is preferably between 1 to 10 KHz. A rectangular wave, a sine wave, a triangular wave, and so forth may be used as a wave form of the vibration bias voltage. A value of the direct-current voltage of the vibration bias voltage is between the electric potential of the background part and the image part, as described above. It is preferable to set the value closer to the potential of the background part than the potential

of the image part from a viewpoint of preventing adhesion of the toner to a potential area of the background part.

When the wave form of the vibration bias voltage is rectangular, it is preferable to set a duty ratio 50 % or less. The duty ratio is a ratio of time when the toner comes closer to the photoconductor during a cycle of the vibration bias. In this way, a difference between a peak value when the toner is directed toward the photoconductor and a time average value of the bias may be increased. Accordingly, movement of the toner becomes further activated. As a result, the toner accurately adheres to a potential distribution of an latent image surface, and surface roughness and resolution may be improved. Further, a difference between a peak value when the carrier having an electric charge having an opposite polarity from the toner is directed toward the photoconductor and a time average value of the bias may be reduced. As a result, movement of the carrier may be controlled. Thus a possibility of the carrier adhering to the background part of the latent image may largely be reduced.

[0096]

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The image forming apparatus according to the present invention is characterized by a charging device. The charging device performs charging by causing a latent image carrier to contact a charging member and applies voltage on the charging member.

(Roller charging)

Fig. 8(a) is a schematic drawing illustrating an example of a configuration of an image forming apparatus using a contact-type charging device. A photoconductor functioning as a charging member or an image carrier is driven to rotate in a direction of an arrow at a predetermined speed (process speed). A charging roller, or a charging member, contacting a photoconductive drum is basically formed of a core metal and a conductive rubber layer concentrically and integrally formed on an outer circumference of the core metal of the roller. Both ends of the core metal are held by a bearing,

and so forth, not shown, so that the core metal may be freely rotate. In addition, a predetermined pressure is applied on the photoconductive drum by a pressing means, not shown. In the figure, the charging roller rotates along with rotation drive of the photoconductor.

The charging roller, designed to have a diameter of 16 mm, is formed of a metal core having a diameter of 9 mm and a rubber layer having a moderate resistance of approximately 100000 Ω · cm coated on the metal core.

A power supply indicated in the figure is electrically connected to the core metal of the charging roller, and a predetermined bias is applied to the charging roller by the power supply. In this way, a circumference surface of the photoconductor is uniformly charged to have a predetermined polarity and an electric potential.

The charging member to be used in the present invention is not particularly limited to, but may be in a form of magnetic brush, a fur brush, and so forth, in addition to a roller. The form of the charging member may be selected according to a specification or an embodiment of an electrophotographic device. In a case of using the magnetic brush, various ferrite particles such as Zn - Cu ferrite, and so forth, are to be used as the charging member, and the magnetic brush is formed of a non-magnetic conductive sleeve for supporting the charging member and a magnetic roller included in the non-magnetic conductive sleeve. In a case of using the fur brush, a fur processed to have conductivity by carbon, cupper sulfide, metal, and metal oxides is used as a material of the fur brush, for instance. The fur is wrapped around or attached to the metal or other metal coil processed to have conductivity to form a charging device.

[0097]

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(Fur brush charging)

Fig. 8(b) is a schematic drawing illustrating a configuration of one example of an image forming apparatus using the contact-type

charging device. A photoconductor functioning as a charged member or an image carrier is driven to rotate in a direction of an arrow at a predetermined speed (process speed). A brush roller formed of the fur brush is designed to contact the photoconductor with a predetermined pressure and a predetermined nip width, prevailing flexibility of a brush part.

A fur brush roller functioning as a contact charging member used in the embodiment is a roll brush an outside diameter of 14 mm and a longitudinal length of 250 mm. A metal core having a diameter of 6 mm also function as an electrode. On the metal core, a tape with a pile of conductive rayon fiber REC-B (manufacturer: Unitika Ltd.), as a brush part, is spirally wrapped around the metal core. A brush of the brush part is formed of a fiber of 300 denier/50 filament, and a density of the fiber is 155 fibers per square millimeter. The roll brush is inserted into a pipe having an inside diameter of 12 mm by rotating the roll brush in a fixed direction so that the brush may be concentric relative to the pipe. Then the roll brush set in the pipe is left in an atmosphere of high temperature and high humidity so that the shape of the fur becomes diagonal.

A resistance value of the fur brush roller is 1 X $10^5~\Omega$ when voltage applied is 100 V. The resistance value is calculated from an electrical current obtained when causing the fur brush roller contacts a metal drum having a diameter of ϕ 30 mm with a nip width of 3 mm and voltage of 100 V is applied on the fur brush roller.

The resistance value of a fur brush charging device is to be 10^4 Ω or more in order to prevent an image defect caused by an insufficient charge of a charging nip part when a low pressure-resistance defect such as a pin hole is developed on the photoconductor functioning as the charged member and a leak current excessively surges into the low pressure-resistance defect. In addition, the resistance value of the fur brush charging device is to be 10^7 Ω or less to sufficiently inject a charge onto a surface of the photoconductor.

Material of the brush fur may include, in addition to REC-B (manufacturer: Unitika Ltd.), REC-C, REC-M1, REC-M10 (manufacturer: Unitika Ltd.), SA-7 (manufacturer: Toray Industries, Inc.), Thunderon (manufacturer: Nihon Sanmo Dyeing Co., Ltd.), Beltron (manufacturer: Kanebo Gohsen, Ltd.), Kuracarbo in which carbon is dispersed in rayon (manufacture: Kuraray Co., Ltd.), Robal (manufacture: Mitsubishi Rayon Co., Ltd.), and so forth. The brush fur is preferably between 3 to 10 denier per fiber, between 10 to 100 filaments/bundle, and between 80 to 600 fibers/ mm². Length of the fur is preferably between 1 to 10 mm.

The fur brush roller is driven to rotate in an opposite (counter) direction to a rotation direction of the photoconductor at a predetermined peripheral velocity (surface velocity), and contacts a face of the photoconductor with speed deference. The power supply applies a predetermined charge voltage to the fur brush roller so that the rotating face of the photoconductor is uniformly charged at a predetermined polarity and potential. In the embodiment, contact charge of the photoconductor by the fur brush roller is dominantly performed by way of direct injection charge, and the surface of the rotating photoconductor is charged at a substantially equal voltage to the charge voltage applied to the fur brush roller.

The charging member used in the present invention may be in a form of, but not limited to, a charging roller, a fur brush, and so forth, in addition to the fur brush roller, and may be selected according to a specification or a form of an electrophotographic device. In a case of using the charging roller, a core metal, on which a rubber layer having a moderate resistance of approximately $100000~\Omega$ ·cm is coated, is generally used. In a case of using the magnetic brush, various ferrite particles such as Zn - Cu ferrite, and so forth, are used as the charging member, and the magnetic brush is formed of a non-magnetic conductive sleeve for supporting the charging member and a magnetic roller included in the non-magnetic conductive sleeve.

[0098]

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(Magnetic brush charger)

Fig. 8(b) is a schematic diagram illustrating a configuration of one example of an image forming apparatus using the contact-type charging device. A photoconductor functioning as a charged member or an image carrier is driven to rotate in a direction of an arrow at a predetermined speed (process speed). A brush roller formed of the magnetic brush is designed to contact the photoconductor with a predetermined pressure and a predetermined nip width, prevailing flexibility of a brush part.

The magnetic brush functioning as the contact charging member used in the present invention is formed of magnetic particles. the magnetic particles, Zn-Cu ferrite particles having an average particle diameter of 25 μ m and Zn-Cu ferrite particles having an average particle diameter of 10 μ m are mixed in a ratio of 1/0.05 so as to form ferrite particles having peaks at each average particle diameter and a total average particle diameter of 25 $\mu\,\mathrm{m}$. ferrite particles are coated with a resin layer having a moderate resistance. The contact charging member is formed of magnetic particles coated with the resin layer prepared as above, a non-magnetic conductive sleeve for supporting the coated magnetic particles, and a magnetic roller included in the non-magnetic conductive sleeve. The coated magnetic particles are coated on the sleeve with a thickness of 1 mm, and consequently, a charging nip having a width of approximately 5 mm is formed between the sleeve and the photoconductor. In addition, a gap between the sleeve holding the magnetic particles and the photoconductor is about 500 $\mu\,\mathrm{m}$. Further, the magnetic roller is rotated so that a surface of the sleeve rubs the surface of the photoconductor at double a speed of and in an opposite direction to a peripheral velocity of the surface of the photoconductor. Thus the photoconductor uniformly contacts the magnetic brush.

The charging member used in the present invention may be in a

form of, but not limited to, a charging roller, a fur brush, and so forth, in addition to the magnetic brush, and may be selected according to a specification or a form of an electrophotographic device. In a case of using the charging roller, a core metal, on which a rubber layer having a moderate resistance of approximately $100000~\Omega$ ·cm is coated, is generally used. In a case of using the fir brush, a fur subjected to conductive processing by carbon, cupper sulfide, metal, and metal oxide is used as a material of the fur brush. The fur is wrapped around or attached to the metal or other metal coil processed to have conductivity to form a charging device.

[0099]

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[Embodiment]

The present invention is further explained according to the following embodiments. However, the present invention is not limited to the embodiments. In the embodiments, part(s) indicates part(s) by weight.

[0100]

Embodiment 1

20 (Synthesis of toner binder)

724 parts of bisphenol A ethylene oxide bimolar adduct, 276 parts of isophthalic acid and 2 parts of dibutyl tin oxide are introduced into a reaction vessel equipped with a condenser tube, a stirrer, and a nitrogen inlet tube, are reacted under normal pressure at 230 °C for 8 hours, are reacted again for 5 hours by decreasing pressure for 10 to 15 mmHg and are cooled to 160 °C. Then 32 parts of phthalic anhydride are added and the reaction is continued for 2 another hours. Next, the reaction mixture is cooled to 80°C, and 188 parts of isohorone diisocyanate is added in ethyl acetate and reacted for 2 hours to obtain pre-polymer (A) containing isocyanate. Next, 267 parts of the pre-polymer (A) and 14 parts of isohorone diamine are reacted at 50 °C for 2 hours to obtain a urea-modified polyester resin (u) having a weight average molecular weight of

64000. Similarly to the above, 724 parts of bisphenol A ethylene oxide bimolar adduct and 276 parts of terephthalic acid are subjected to polycondensation at 230 °C for 8 hours, and are reacted for 5 hours by decreasing pressure for 10 mmHg to 15mmHg to obtain non-modified polyester (a) having a peak molecular weight of 5,000. 200 parts of the urea-modified polyester resin (1) and 800 parts of the non-modified polyester resin (a) are dissolved and mixed in 2,000 parts of ethyl acetate/MEK (1/1) mixed solvent to obtain an ethyl acetate/MEK solution of the toner binder (1). The resulting mixture is dried under partially reduced pressure to isolate the toner binder (1). In this case, Tg is 62°C, an acid value is 4.2 KOHmg/g, and a peak molecular weight is 4,500.

[0101]

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(Production of toner)

240 parts of an ethyl acetate/MEK solution of the toner binder (1), 5 parts of ester wax as wax (acid value: 3) and 8 parts of carbon black (BP1300, manufacturer: Cabot Corporation) introduced into a beaker, and stirred at 12,000 rpm at 60 $^{\circ}\mathrm{C}$ by a TK homomixer to uniformly dissolve and disperse the ingredients. 706 parts of ion exchange water, 294 parts of a 10% suspension of hydroxyapatite (Supertite 10, manufacture: Japan Industries) and 0.2 parts of a sodium dodceyl benzene sulfonate are introduced into the beaker, and are uniformly dissolved. Next, the temperature is raised to 60°C , and the above toner material solution is introduced while stirring at 12,000 rpm by the TK homomixer for 10 minutes. Then, the solution is left to stand for 2 hours for stabilization. Next, the mixed solution is transferred to a flask equipped with a stirring rod and a thermometer, and the temperature is raised to 98 °C to remove the solvent. Subsequently, the product is filtered, rinsed, and dried, and then graded by air power to obtain toner particles having an average particle diameter of 6.3 μ m (volume average particle diameter Dv/number average particle diameter Dn : 1.14), and a circularity of 0.97. Next, 0.5

parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide are added to 100 parts of the toner particles and mixed in a Henschel mixer to obtain the toner (1) according to the present invention. In the toner, an occupied area ratio of the wax is 20 (%) in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 86% by number, and the wax particles having a dispersion diameter of 0.1 to 3.0 $\mu\rm m$ are 88% by number. An evaluation result is shown in Table 1.

[0102]

15 Embodiment 2

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(Synthesis of toner binder)

Similar to the embodiment 1, 334 parts of bisphenol A ethylene oxide bimolar adduct, 334 parts of bisphenol A propylene oxide bimolar adduct, 274 parts of isophthalic acid, and 20 parts of anhydrous trimellitic acid are subjected to polycondensation, and then reacted with 154 parts of isohorone diisocyanate to obtain a pre-polymer (2). Next, 213 parts of the prepolymer (2), 9.5 parts of isohorone diamine and 0.5 parts of dibutylamine are reacted in the same way as in the embodiment 1 to obtain urea-modified polyester (2) having a weight average molecular weight of 52,000. 200 parts of the urea-modified polyester (2) and 800 parts of the non-modified polyester (a) are dissolved and mixed in 2,000 parts of ethyl acetate/MEK (1/1) mixed solvent, to obtain an ethyl acetate solution of the toner binder (2). A part of the solution is dried under reduced pressure to isolate the toner binder (2). Tg is 65°C, the acid value is 10, and the peak molecular weight is 5500.

[0103]

(Production of toner)

The identical procedure as the procedure of the embodiment 1 is used except that the ester wax is replaced by 7 parts of de-free fatty acid carnauba wax (acid value: 1.5) and is used as wax, and the dissolution temperature and dispersion temperature are changed to 50 $^{\circ}$ C to obtain the toner (2) according to the present invention having a particle diameter of 5.8 μ m (Dv/Dn: 1.11) and a circularity of 0.98. In the toner, an occupied area ratio of the wax is 30 (%) in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 79 % by number, and the wax particles having a dispersion diameter of 0.1 to 3.0 μ m are 90 % by number. An evaluation result is shown in Table 1.

[0104]

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Comparative example 1

(Synthesis of toner binder)

354 parts of bisphenol A ethylene oxide bimolar adduct and 166 parts of isophthalic acid are subjected to polycondensation using 2 parts of dibutylene oxide as a catalyst to obtain a comparative toner binder (1) having a weight average molecular weight of 8,000. Tg, an acid value, and a peak molecular weight the comparative toner binder (1) are 57 $^{\circ}$ C, 15, and 6000, respectively.

[0105]

(Production of toner)

100 parts of the toner binder (1), 200 parts of an ethyl acetate solution, 10 parts of carbon black (BP1300, manufacturer: Cabot Corporation), and 10 parts of polypropylene are introduced into a beaker, and stirred at 12,000 rpm at 50 $^{\circ}$ C by a TK homomixer to uniformly dissolve and disperse the ingredients. Then the toner is prepared in the same manner as in the embodiment 1. Thus

comparative toner (1) having a volume average particle diameter of 6.0 $\mu\rm m$ (Dv/Dn: 1.36) and a circularity of 0.95 is obtained. In the toner, an occupied area ratio of the wax is 3 (%) in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 55 % by number, and most part of the rest of the wax particles exists inner part of the particle. The wax particles having a dispersion diameter of 0.1 to 3.0 $\mu\rm m$ are 63 % by number. An evaluation result is shown in Table 1.

[0106]

15 [Table 1]

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	<u> </u>	I - :		Г	1	· ·
Occupied area		Lowest	Hot	Heat	Range	Wax/
ratio of the wax	fluidity	fixing	(℃)	resistant	of	resin
in a portion on an		temperature	8	storage	fixing	
arbitral cross-		(°C)		stability	temp.	
section having a					(℃)	
center of the						
toner particle						
thereon, wherein						
the portion is						
positioned						
between a						
circumference of						
the arbitral						
cross-section and				•		
an inner						
circumference				:		
having a radius						
which is						
two-thirds of the		:				
radius of the						
toner particles						

	(%)						
Emb.	20	0.27	110	210	0	100	5/80
1							
Emb.	30	0.25	120	230	0	110	5/80
2				or			
				more			
Com.	3	0.27	140	170	Δ	3.0	10/100
1							

[0107]

Embodiment 3

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(Production example of pre-polymer)

724 parts of bisphenol A ethylene oxide bimolar adduct, 250 parts of isophthalic acid, 24 parts of terephthalic acid, and 2 parts of dibutylene oxide are introduced in a reaction vessel equipped with a condenser tube, a stirrer, and a nitrogen supply tube. Then the ingredients are reacted at 230 °C under normal pressure for 8 hours. Thereafter, the resulted mixture is further reacted under a reduced pressure of 10 mmHg to 15 mmHg for 5 hours while dewatering. The reaction mixture is then cooled to 160 °C and 32 parts of phthalic anhydride is added in the reaction mixture to react for 2 hours. The reaction mixture is further cooled to 80°C, and is reacted with 188 parts of isophorone diisocyanate in ethyl acetate for 2 hours. A pre-polymer (3) containing an isocyanate group having a weight average molecular weight of 12000 is thus produced.

[0108]

(Production example of Ketimine compound)

30 parts of isophorone diamine and 70 parts of methylethyl ketone are introduced into a reaction vessel equipped with a stirring rod and a thermometer, and then reacted at 50 $^{\circ}$ C for 5 hours to obtain a ketimine compound (1).

[0109]

25 (Production example of non-modified polyester)

Similar to the above, 724 parts of bisphenol A ethylene oxide

bimolar adduct and 276 parts of terephthalic acid are subjected to polycondensation at 230 $^{\circ}$ C under normal pressure for 6 hours. Thereafter, the resulted mixture is further reacted under a reduced pressure of 10 mmHg to 15 mmHg for 5 hours while dewatering. Thus the non-modified polyester (b) having a peak molecular weight of 6000 and an acid value of 3.8 is obtained.

[0110]

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(Production example of toner)

15.4 parts of the pre-polymer (1), 64 parts of the polyester (b) and 78.6 parts of ethyl acetate are introduced into a beaker, and then the ingredients are stirred and dissolved. Next, 8 parts of rice wax functioning as wax, and 4 parts of copper phthalocyanine blue are added and stirred at 12,000 rpm at 60 $^{\circ}$ C by a TK homomixer to uniformly dissolve and disperse the ingredients. Then, 2.7 parts of the ketimine compound (1) is added and dissolved to obtain a toner material solution (1). 706 parts of ion exchange water, 294 parts of a 10% suspension of hydroxyapatite (Supertite 10, manufacture: Japan Chemical Industries) and 0.2 parts of a sodium dodceyl benzene sulfonate are introduced into the beaker, and are uniformly dissolved. Next, the temperature is raised to 60° C, and the above toner material solution (1) is introduced while stirring at 12,000 rpm by the TK homomixer for 10 minutes. Thereafter, the mixed solution is left to stand for 2 hours to stabilize. Next, the mixed solution is transferred to a flask equipped with a stirring rod and a thermometer, and the temperature is raised to 98 $^{\circ}{
m C}$ to remove the solvent by causing a urea reaction. Subsequently, the product is filtered, rinsed, and dried, and then graded by air power to obtain toner particles having an average particle diameter of 4.3 μ m. Next, 0.5 parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide are added to 100 parts of the toner particles and mixed in a Henschel mixer to obtain the toner (5) according to the present invention. (Dv/Dn : 1.08), circularity 0.94, peak molecular weight 6000, and Tg 62 $^{\circ}$ C are obtained. In the toner, an occupied area ratio of the wax is 20 (%) in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 90 % by number, and the wax particles having a dispersion diameter of 0.1 to 3.0 $\mu\rm m$ are 88 % by number. An evaluation result is shown in Table 2.

[0111]

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Embodiment 4

(Production example of prepolymer)

Similar to the embodiment 1, 669 parts of bisphenol A ethylene oxide bimolar adduct, 274 parts of isophthalic acid, and 20 parts of trimellitic anhydride are subjected polycondensation, and thereafter the resulted product is reacted with 154 parts of isophorone diisocyanate to obtain pre-polymer (4) having a volume average molecular weight of 15,000.

[0112]

(Production example of toner)

15.5 parts of the pre-polymer (2), 64 parts of polyester (b) and 78.8 parts of ethyl acetate are introduced into a beaker, and are stirred and dissolved. Next, 5 parts of montan wax functioning as wax, and 4 parts of copper phthalocyanine blue are added and stirred at 12,000 rpm at 50 °C by a TK homomixer to uniformly dissolve and disperse the ingredients. Finally, 2.4 parts of the ketimine compound (1) and 0.036 parts of dibutyl amine are added and dissolved to obtain a toner material solution (2). The identical procedure as the procedure in the embodiment 3 is used except that the toner material solution (1) is replaced by the toner material solution (2), and the dispersion temperature is changed to 50 °C to obtain the toner (6) according to the present invention having a volume average particle diameter of 7.2 μ m (Dv/Dn: 1.15), and a

circularity of 0.98. In the toner, an occupied area ratio of the wax is 25 (%) in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 92 % by number, and the wax particles having a dispersion diameter of 0.1 to 3.0 μ m are 94 % by number. Tg is 60 °C and the peak molecular weight is 4000. An evaluation result is shown in Table 2.

[0113]

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Embodiment 5

The identical procedure as the procedure of the embodiment 4 is used except that the amount of the montan wax is changed from 5 parts, as in the embodiment 1, to 6.5 parts, and the time for standing is changed from 2 hours to 30 minutes to obtain the toner (7) according to the present invention having a volume average particle diameter of 6.7 μ m (Dv/Dn: 1.19), and a circularity of 0.98.

[0114]

Comparative example 2

(Synthesis of toner binder)

354 parts of bisphenol A ethylene oxide bimolar adduct and 166 parts of terephthalic acid are subjected to polycondensation using 2 parts of dibutylene oxide as a catalyst to obtain a comparative toner binder (2) having a peak molecular weight of 8,000.

[0115]

(Production example of toner)

100 parts of the comparative toner binder (2), 200 parts of an ethyl acetate, 4 parts of copper phthalocyanine blue, and 5 parts of polypropylene are introduced into a beaker, and stirred at 12,000 rpm at 50 $^{\circ}$ C by a TK homomixer to uniformly dissolve and disperse the ingredients. Thus a comparative toner material solution is

obtained. Thereafter, the toner is produced in the same manner as in the embodiment 4, and comparative toner (2) having a volume average particle diameter of 6.9 μ m (Dv/Dn: 1.45) and a circularity of 0.94 is obtained. In the toner, an occupied area ratio of the wax is 45 (%) in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, the wax not existing on the surface of the toner particle but existing adjacent to the surface of the toner particle are 65 % by number, and most part of the rest of the wax particles are exposed on the surface of the toner the particles. The wax particles having a dispersion diameter of 0.1 to 3.0 μ m are 68 % by number. An evaluation result is shown in Table 2.

[0116] [Table 2]

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Emb.	toner particles (%) 20	0.26	130	220	0	90	8/79.4
	of the radius of the						
	which is two-thirds						:
	having a radius						
	circumference						
	section and an inner						
	arbitral cross-						
	circumference of the						
	between a						
	is positioned				8		
	wherein the portion						
	particle thereon,						
	center of the toner						
	section having a					(℃)	
	arbitral cross-		(°C)		stability	temp.	
	in a portion on an		temperature		storage	fixing	
	of the wax	fluidity	fixing	(℃)	resistant	of	resin
	Ooccupied area ratio	Particle	Lowest	Hot	Heat	Range	Wax/

3							
Emb.	25	0.29	120	230	0	110	5/79.5
4				or			
	:			more			
Emb.	35	0.24	120	210	0	90	6.5/79.5
5							
Com.	45	0.16	150	230	×	80 .	5/100
2				or			
				more			

[0117]

(Measuring method)

(1) Particle diameter distribution

At first, 0.1 to 5 ml of a surfactant (preferably alkylbenzene sulfonate) functioning as a dispersant is added to 100 to 150 ml of an electrolytic solution. The electrolytic solution is prepared from 1 % NaCl solution of primary sodium chloride. In this case, for example, ISOTON-II (manufacturer: Beckman Coulter, Inc.) may be used. Further, 2 to 20 mg of a test portion is added to the electrolytic solution. The electrolytic solution suspending the test portion is dispersed by an ultrasonic disperser for about 1 to 3 minutes. Thereafter, toner particles or toner volume, number of toner are measured by the above-mentioned measuring apparatus using an aperture of 100 $\mu\,\mathrm{m}$. Thus a volume particle distribution and number particle distribution are calculated.

[0118]

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As channels, 13 channels of between 2.00 to less than 2.52 μ m, between 2.52 to less than 3.17 μ m, between 3.17 to less than 4.00 μ m, between 4.00 to less than 5.04 μ m, between 5.04 to less than 6.35 μ m, between 6.35 to less than 8.00 μ m, between 8.00 to less than 10.08 μ m, between 10.08 to less than 12.70 μ m, between 12.70 to less than 16.00 μ m, between 16.00 to less than 20 μ m, between 20.20 to less than 25.04 μ m, between 25.40 to less than 32.00 μ m, and between 32.00 to less than 40.30 μ m are used. A particle

having a particle diameter of 2.00 or more to less than 40.30 μ m are applied. A ratio Dv/Dn is calculated from a volume average particle diameter (Dv) of volume reference obtained from the volume particle distribution relating to the present invention, and a number average particle diameter (Dn) obtained from the number particle distribution.

[0119]

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(2) Circularity

An optical detection band method suitable a method of measuring In the method, particle-containing suspension is passed through a photographic detection band on a plate, and a particle image is optically detected by/analyzed with a CCD camera. It is found that the toner having an average circularity of 0.960 or more may be effective in forming a high-resolution image with appropriate The average circularity of 0.960 is density reproducibility. obtained by the method by dividing a circumference length of a circle having a substantially equal projected area by a circumference length of an existing particle, and the toner having the average circularity of 0.980 or more is determined to be effective to form a high definition image with appropriate reproducibility and toner density. The toner is preferably have an average circularity of 0.980 to 1.000. The value is measured as the average circularity by a flow type particle image analyzer FPIA-2000. Specifically, 0.1 to 5 ml of a surfactant, preferably alkylbenzene sulfonate, functioning as a dispersant is added to 100 to 150 ml of water in a vessel in which a solid impurity is removed beforehand. Further, 0.1 to 0.5 g of a test portion is added to the water. The suspension in which the test portion is dispersed is subjected to dispersal processing for about 1 to 3 minutes by the ultrasonic disperser. In this case, the concentration of the dispersion liquid is set to 3000 to 10000 number/ μ l, and the shape and the distribution of the toner is measured by the apparatus.

[0120]

(3) Particle fluidity

Powder density of the toner is measured by using a Powder Tester (manufacture: Hosokawa Micron Corporation). The better fluidity of toner is, the more powder density of the toner is.

5 [0121]

(4) Lowest fixing temperature ($^{\circ}$ C)

A copying test is carried out on Type-6200 paper manufactured by Ricoh Company, Ltd., by using a modified fixing device of a copier imagio NEO 450 manufactured by Ricoh Company, Ltd., as a fixing roller. The lowest fixing temperature is defined as temperature at which a residual rate of the image density is 70 % or more after rubbing a fixing image with a pad. A metal cylinder of the fixing roller is formed of a Fe material and has a thickness of 0.34 mm. In addition, a surface pressure is set to 1.0 X 10⁵ PA.

[0122]

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(5) Temperature at which hot offset occurs (HOT)

Fixing is evaluated similar to the lowest fixing temperature, and occurrence of hot offset to the fixing image is visually evaluated. The temperature at which the hot offset occurs is defined as temperature of the fixing roller at which the hot offset occurs.

[0123]

(6) Hest-resistant storage stability

Hest-resistant storage stability is defined as a residual rate of the toner stored at 50 $^{\circ}$ C for 8 hours and then put through a sifter of a 42 mesh. The better the heat-resistant storage stability, the less the residual ratio is. The heat-resistant storage stability is evaluated using the residual ratio on a scale of one to 10 as follows.

X: 30 % or more

△: 20 to 30 %

O: 10 to 20 %

◎: less than 10 %

[0124]

Embodiment 6

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(Production example of toner)

15 parts of the pre-polymer (1), 85 parts of polyester (c) and 100 parts of ethyl acetate are put into a beaker, and are stirred and dissolved. Next, 9 parts of carnauba wax and 4 parts of copper phthalocyanine blue are added and stirred in the beaker at 12,000 rpm at 60 $^{\circ}$ C by a TK homomixer to uniformly dissolve and disperse the ingredients. Finally, 2.7 parts of the ketimine compound (1) is added and dissolved in the beaker to obtain a toner material solution (1). 706 parts of ion exchange water, 294 parts of a 10% suspension of hydroxyapatite (Supertite 10, manufacture: Japan Chemical Industries) and 0.2 parts of a sodium dodceyl benzene sulfonate are introduced into the beaker, and are uniformly dissolved. Next, the temperature is raised to 60° C, and the above toner material solution is introduced while stirring at 12000 rpm by the TK homomixer for 10 minutes. Thereafter, the mixed solution is left to stand at 40 $^{\circ}\mathrm{C}$ for 5 minutes. Next, the mixed solution is transferred to a flask equipped with a stirring rod and a thermometer, and the temperature is raised to 98 $^{\circ}{\text{C}}$ remove the solvent while inducing urea reaction. Subsequently, the product is filtered, cleaned and dried, and graded by air power to obtain toner particles. The volume average particle diameter of the toner particles is 6 μ m. Next, 0.5 parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide are added to 100 parts of the toner particles and mixed by a Henschel mixer to obtain the toner (6) according to the present invention. In the toner, an occupied area ratio of the wax is 12 (%) in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, and a ratio of the wax exists adjacent to the surface of the toner particle and inner part of the toner particle is 5 : 4. The wax particles having a dispersion diameter of 0.1 to 3.0 μ m are 85 % by number. The particle diameter 6.0 μ m (Dv/Dn : 1.08), the circularity 0.97, the peak molecular weight 6000, and Tg 62 °C are obtained. An evaluation result is shown in Table 3.

[0125]

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Embodiment 7

(Production example of toner)

15 parts of the pre-polymer (1), 85 parts of the polyester (c), and 100 parts of the ethyl acetate are introduced into a beaker, and are stirred and dissolved. Next, 8 parts of carnauba wax and 4 parts of copper phthalocyanine blue are added and stirred at 12,000 rpm at 60 $^{\circ}$ C by a TK homomixer to uniformly dissolve and disperse the ingredients. Then, 2.7 parts of the ketimine compound (1) is added and dissolved to obtain a toner material solution (1). 706 parts of ion exchange water, 294 parts of a 10% suspension of hydroxyapatite (Supertite 10, manufacture: Japan Chemical Industries) and 0.2 parts of a sodium dodecylbenzene sulfonate are put into the beaker, and uniformly dissolved. Next, the temperature is raised to $60\,^{\circ}\mathrm{C}$, and the above toner material solution is introduced while stirring at 12,000 rpm by the TK homomixer for 10 minutes. Thereafter, the mixed solution is left to stand at 40 $^{\circ}\mathrm{C}$ for 30 minutes. Then, the mixed solution is transferred to a flask equipped with a stirring rod and a thermometer and the temperature is raised to 98 $^{\circ}$ C to remove the solvent while inducing urea reaction. Subsequently, the product is filtered, cleaned and dried, and graded by air power to obtain toner particles. The volume average particle diameter of the toner particles is 6 $\mu\,\mathrm{m}$. Next, 0.5 parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide are added to 100 parts of the toner particles and mixed by a Henschel mixer to obtain the toner (7) according to the present invention. In the toner, an occupied area ratio of the wax is 12 (%) in a portion

on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, and a ratio of the wax exists adjacent to the surface of the toner particle and inner part of the toner particle is 5 : 3. The wax particles having a dispersion diameter of 0.1 to 3.0 μ m are 82 % by number. The particle diameter 6.1 μ m (Dv/Dn : 1.08), the circularity 0.98, the peak molecular weight 6000, and Tg 62 °C are obtained. An evaluation result is shown in Table 3.

[0126]

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Embodiment 8

(Production example of toner)

15 parts of the pre-polymer (1), 85 parts of the polyester (c), and 100 parts of the ethyl acetate are introduced into a beaker, and are stirred and dissolved. Next, 7 parts of carnauba wax and 4 parts of copper phthalocyanine blue are added and stirred at 12,000 rpm at 60 °C by a TK homomixer to uniformly dissolve and disperse the ingredients. Finally, 2.7 parts of the ketimine compound (1) is added and dissolved to obtain a toner material solution (1). 706 parts of ion exchange water, 294 parts of a 10% suspension of (Supertite 10, manufacture: Japan Chemical hydroxyapatite Industries) and 0.2 parts of a sodium dodecylbenzene sulfonate are introduced into the beaker, and uniformly dissolved. Next, the temperature is raised to 60° C, and the above toner material solution (1) is introduced while stirring at 12,000 rpm by the TK homomixer for 10 minutes. Thereafter, the mixed solution is left to stand at 40 °C for 60 minutes. Next, this mixed solution is transferred to a flask equipped with a stirring rod and a thermometer, and the temperature is raised to 98 °C to remove the solvent while inducing urea reaction. Subsequently, the product is filtered, cleaned and dried, and graded by air power to obtain toner particles. Next,

0.5 parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide are added to 100 parts of the toner particles and mixed by a Henschel mixer to obtain the toner (8) according to the present invention. In the toner, an occupied area ratio of the wax is 12 (%) in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, and a ratio of the wax exists adjacent to the surface of the toner particle and inner part of the toner particle is 5 : 2. The wax particles having a dispersion diameter of 0.1 to 3.0 μ m are 86 % by number. The particle diameter 5.9 μ m (Dv/Dn: 1.06), the circularity 0.97, the peak molecular weight 6000, and Tg 62 $^{\circ}$ C are obtained. An evaluation result is shown in Table 3.

[0127]

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Embodiment 9

(Production example of toner)

15 parts of the pre-polymer (1), 85 parts of the polyester (c), and 100 parts of the ethyl acetate are introduced into a beaker, and are stirred and dissolved. Next, 6 parts of carnauba wax and 4 parts of copper phthalocyanine blue are added and stirred at 12,000 rpm at 60 $^{\circ}$ C by a TK homomixer to uniformly dissolve and disperse the ingredients. Finally, 2.7 parts of the ketimine compound (1) is added and dissolved to obtain a toner material solution (1). 706 parts of ion exchange water, 294 parts of a 10% suspension of Chemical hydroxyapatite (Supertite 10, manufacture: Japan Industries), and 0.2 parts of a sodium dodecylbenzene sulfonate are introduced into the beaker, and uniformly dissolved. Next, the temperature is raised to 60° C, and the above toner material solution (1) is introduced while stirring at 12,000 rpm by the TK homomixer for 10 minutes. Thereafter, the mixed solution is left to stand at 40 $^{\circ}\mathrm{C}$ for 90 minutes. Next, the mixed solution is transferred to a flask equipped with a stirring rod and a thermometer, and the temperature is raised to 98 $^{\circ}\mathrm{C}$ to remove the solvent while inducing urea reaction. Subsequently, the product is filtered, cleaned and dried, and graded by air power to obtain toner particles. Next, 0.5 parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide are added to 100 parts of the toner particles and mixed by a Henschel mixer to obtain the toner (9) according to the present invention. In the toner, an occupied area ratio of the wax is 12 (%) in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, and a ratio of the wax exists adjacent to the surface of the toner particle and inner part of the toner particle is 5:1. The wax particles having a dispersion diameter of 0.1 to 3.0 μ m are 85 % by number. The particle diameter 6.3 μ m (Dv/Dn : 1.08), the circularity 0.96, the peak molecular weight 6000, and Tg 62 $^{\circ}$ C are obtained. An evaluation result is shown in Table 3. [0128]

Comparative example 3

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20 (Production example of toner)

15 parts of the pre-polymer (1), 85 parts of the polyester (c), and 100 parts of the ethyl acetate are introduced into a beaker, and are stirred and dissolved. Next, 5 parts of carnauba wax, and 4 parts of copper phthalocyanine blue are added and stirred at 12,000 rpm at 60 °C by a TK homomixer to uniformly dissolve and disperse the ingredients. Finally, 2.7 parts of the ketimine compound (1) is added and dissolved to obtain a toner material solution (1). 706 parts of ion exchange water, 294 parts of a 10% suspension of hydroxyapatite (Supertite 10, manufacture: Japan Chemical Industries), and 0.2 parts of a sodium dodecylbenzene sulfonate are introduced into the beaker, and are uniformly dissolved. Next, the temperature is raised to 60°C, and the above toner material solution (1) is introduced while stirring at 12,000 rpm by the TK

homomixer for 10 minutes. Thereafter, the mixed solution is left to stand at 50 $^{\circ}\mathrm{C}$ for 60 minutes. Next, the mixed solution is transferred to a flask equipped with a stirring rod and a thermometer, the temperature is raised to 98 $^{\circ}{\rm C}$ to remove the solvent while inducing urea reaction. Subsequently, the product is filtered, cleaned, and dried, and graded by air power to obtain toner particles. Next, 0.5 parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide str added to 100 parts of the toner particles and mixed by a Henschel mixer to obtain comparative toner (3) according to the present invention. In the toner, an occupied area ratio of the wax is 12 (%) in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, and a ratio of the wax exists adjacent to the surface of the toner particle and inner part of the toner particle is 5:0. The wax particles having a dispersion diameter of 0.1 to 3.0 μ m are 92 % by number. The particle diameter 6.2 μ m (Dv/Dn : 1.08), the circularity 0.97, the peak molecular weight 6000, and Tg 62 $^{\circ}$ C are obtained. An evaluation result is shown in Table 3.

[0129]

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Comparative example 4

(Production example of toner)

15 parts of the pre-polymer (1), 85 parts of polyester (c) and 100 parts of ethyl acetate are introduced into a beaker, and are stirred and dissolved. Next, 10 parts of carnauba wax, and 4 parts of copper phthalocyanine blue are added and stirred at 12,000 rpm at 60 °C by a TK homomixer to uniformly dissolve and disperse the ingredients. Finally, 2.7 parts of the ketimine compound (1) is added and dissolved to obtain a toner material solution (1). 706 parts of ion exchange water, 294 parts of a 10% suspension of hydroxyapatite (Supertite 10, manufacture: Japan Chemical Industries), and 0.2

parts of a sodium dodecylbenzene sulfonate are introduced into the beaker, and are uniformly dissolved. Next, the temperature is raised to $60\,^{\circ}\mathrm{C}$, and the above toner material solution (1) is introduced while stirring at 12,000 rpm by the TK homomixer for 10 minutes. Next, the mixed solution is transferred to a flask equipped with a stirring rod and a thermometer, and the temperature is raised to 98 $^{\circ}{\rm C}$ to remove the solvent while inducing urea reaction. Subsequently, the product is filtered, cleaned and dried, and graded by air power to obtain toner particles. Next, 0.5 parts of hydrophobic silica and 0.5 parts of hydrophobic titanium oxide are added to 100 parts of the toner particles and are mixed by a Henschel mixer to obtain the comparative toner (4) according to the present invention. In the toner, an occupied area ratio of the wax is 12 (%) in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles, and a ratio of the wax exists adjacent to the surface of the toner particle and inner part of the toner particle is 5 : 5. The wax particles having a dispersion diameter of 0.1 to 3.0 μ m are 77 % by number. The particle diameter 6.1 μ m (Dv/Dn: 1.08), the circularity 0.96, the peak molecular weight 6000, and Tg 62 $^{\circ}$ C are obtained. An evaluation result is shown in Table 3. [0130]

25 [Table 3-1]

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	Emb. 1	Emb. 2	Emb. 3	Emb. 4	Emb. 5	Comp. 1	Comp. 2
Amount of	86	79	90	92	65	55	65
wax adjacent							
to toner							
surface (%)							
(Remark 1)							
Amount of	14	21	10	8	35	45	0
wax in the							
toner (%)							

(Remark	2)							
Others								Exposed
								to the
								surface
Total		5	7	10	8	6.5	10	5
amount	of						1	
wax								
Amount	of	120	120	79.4	79.5	79.5	110	100
resin						-		
Toner		None	None	None	None	None		Occurred
fusion		•						
Range	of	100	110	110	90	90	30	80
fixing								
temperat	ure							
(°C)								

[0131] [Table 3-2]

	Emb. 6	Emb. 7	Emb. 8	Emb. 9	Comp. 3	Comp. 4
Amount of	5	5	5	5	5	5
wax adjacent						
to toner						i
surface (%)						
(Remark 1)						
Amount of	4	3	2	1	0	5
wax in the						
toner (%)						
(Remark 2)						
Total	9	8	7	6	5	10
amount of						
wax			_			
Amount of	100	100	100	100	100	100
resin						
Toner	none	none	none	none	none	Occurred
fusion						
Range of	110	100	100	90	45	110
fixing		, ·				
temperature						
(℃)						

(Remark 1): an amount of wax existing adjacent to the surface of the toner is a ratio of an number of wax particles existing in a portion on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between a circumference of the arbitral cross-section and an inner circumference having a radius which is two-thirds of the radius of the toner particles

(Remark 2): an amount of wax existing inner part of the toner particle is a ratio of a number of wax particles existing in a portion formed on an arbitral cross-section having a center of the toner particle thereon, wherein the portion is positioned between an inner circumference having a radius which is two-thirds of the radius of the toner particle.

For the purpose of adjusting a variation in a wax distribution between the toner particles, an average value is obtained from 10 pieces of toner particles of each of the embodiments and the comparative examples.

A ratio of the amount of wax in the toner and the amount of wax adjacent to the surface of the toner particle, as in the table, is 2.27 times as much, relative to a cross-section area, and 1.37 times as much relative to volume.

It is proved from the above result that the ratio of the amount of the wax adjacent to the surface of the toner particle to the amount of the wax in the toner is preferably between 50: 40 to 50: 5, and more preferably between 50: 30 to 50: 10.

[0132]

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(Evaluation of toner fusion)

Thus produced toner is set in a modified My Copy M-5 (manufacturer: Ricoh Company, LTD.). Printing is performed 10,000 times using a manuscript having an image area ratio of 6 %. Thereafter, the occurrence of toner fusion on a surface of a developing roller for a one component developer and the toner

deposition to a toner thickness-regulating member are evaluated.

[0133]

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[Effects of the Invention]

As is obvious from detailed and specific explanation described above, in a fixing device of low energy consumption, toner having a wide fixing and releasing width, and excellent storage stability may be achieved. In this case, the toner is resistant to crack and a property of the toner does not change much when a toner particle cracks. In addition, an efficient production method of such toner having a wide fixing area and which may achieve a high quality image may be achieved. Further, in a case when the toner is used as color toner, excellent glossiness and hot offset resistance may be achieved. Accordingly, it is not necessary to apply oil on a fixing roller. Furthermore, excellent effect of achieving an image with high-resolution and high-definition may be achieved.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 is a drawing illustrating relation between a major axis, a minor axis, and a thickness of an example of a toner particle according to the present invention.

[Fig. 2]

Fig. 2 is a schematic drawing illustrating an example of a fixing device of an image forming apparatus according to the present invention.

25 [Fig. 3]

Fig. 3 is a drawing illustrating an example of an image forming apparatus according to the present invention.

[Fig. 4]

Fig. 4 is a schematic drawing illustrating a configuration of an example of an image forming apparatus including a process cartridge according to the present invention.

[Fig. 5]

Fig. 5 is a frame format illustrating a layer configuration of

an example of a photoconductor according to the present invention.

[Fig. 6]

Fig. 6 is a drawing illustrating an example of a development device according to the present invention.

5 [Fig. 7]

Fig. 7 is a drawing illustrating an example of a charging characteristic of contact charge.

[Fig. 8]

Fig. 8(a) and Fig. 8(b) are drawings illustrating examples of a roller contact charging device and a brush contact charging device, respectively.

[Reference Numerals]

- 1 Fixing roller
- 2 Pressing roller
- 15 3 Metal cylinder
 - 4 Offset inhibiting layer
 - 5 Heating lamp
 - 6 Metal cylinder
 - 7 Offset inhibiting layer
- 20 8 Heating lamp
 - T Toner image
 - S Support body (transfer paper such as paper)
 - 10 Process cartridge
 - 11 Photoconductor
- 25 12 Charging means
 - 13 Development means
 - 14 Cleaning means
 - 20 Development part
 - 21 Development sleeve
- 30 22 Power supply
 - 23 Development part
 - 24 Photoconductive drum
 - 500 Electrophotographic photoconductor

- 501 Support body
- 502 Photoconductive layer
- 503 Surface layer

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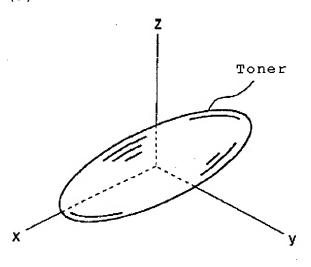
- 504 Charge injection inhibiting layer
- 5 505 Electric charge generating layer
 - 506 Electric charge transport layer
 - [Selected Drawing] Fig. 1

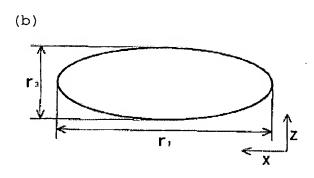
10 [Name of Document] Abstract of the Disclosure
[Abstract]

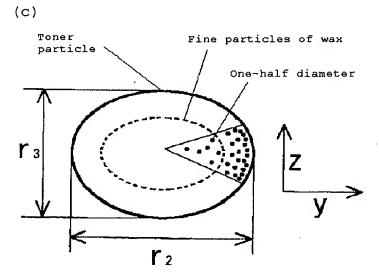
[Objectives of the Invention] It is an object of the present invention to provide toner which has improved fixing ability at low temperature and offset resistance with low electric power consumption, forms a high quality toner image, and has long-term excellent storage stability, to provide toner which may achieve a high quality image and has a wide fixing area, further, in a case of color toner, to provide toner excellent in glossiness and hot offset resistance, to provide toner capable of forming a high-resolution image, to provide, when the toner is used in a high-speed apparatus, toner which may achieve a balance between prevention of toner fusion by running an appropriate amount of wax and an excellent fixing ability during a fixing process even when the toner is crushed by being subjected to a mechanical impact between the toner and a carrier particle, a development member, and so forth, during a development process, and to provide an image forming apparatus using the toner and a process cartridge which is attachable to or detachable from the image forming apparatus. [Means for Achieving the Objectives] Dry toner including at least a toner binder, a colorant, and wax, characterized in that the wax is included in a toner particle in a form of fine particle and exists throughout a part adjacent to a surface and an inner part of the toner particle, and density of the wax existing adjacent to the surface of the toner particle is greater than density of the wax existing in the inner part of the toner particle.

NOV:18 7005 [Name of Document] [Fig. 1] (a)

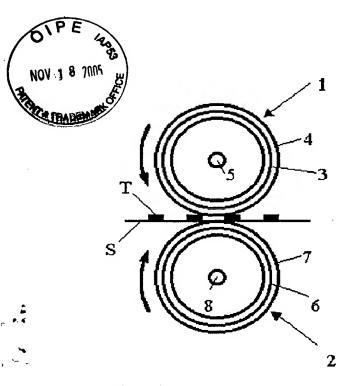
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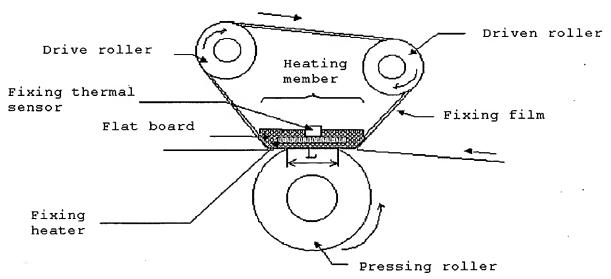


[Fig. 2]

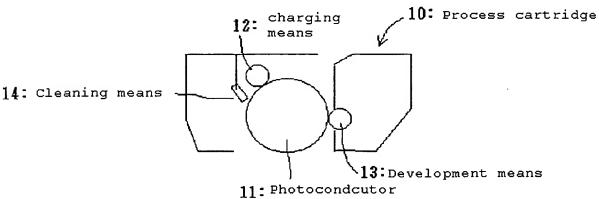


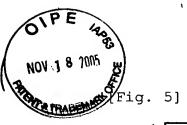
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[Fig. 3]

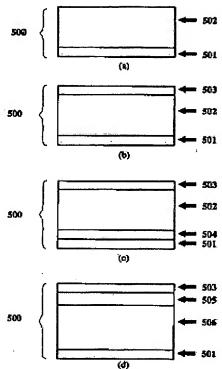


[Fig. 4]

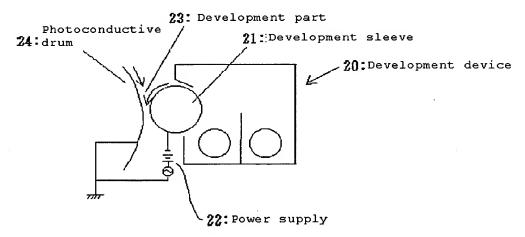




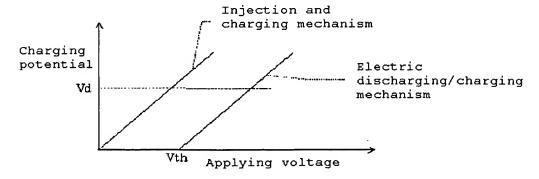
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[Fig. 6]



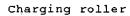
[Fig. 7]

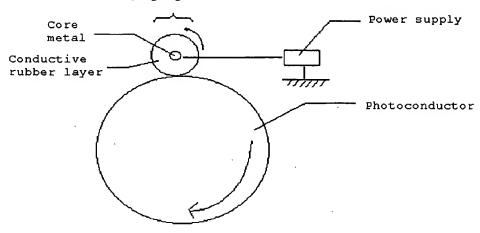


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[Fig. 8]

(a)





(b)

